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Efficient photovoltaic cell for solar energy conversion - having titanium dioxide layer coated with photosensitive dye in contact with redox electrolyte system

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Patent Family:

Patent No	Kind	Date	Applicat No	Kind	Date	Week	
WO 9116719	A	19911031				199146	B
AU 9177483	A	19911111				199207	
EP 525070	A1	19930203	EP 91908382	A	19910417	199305	
			WO 91EP734	A	19910417		
JP 5504023	W	19930624	JP 91507923	A	19910417	199330	
			WO 91EP734	A	19910417		
AU 650878	B	19940707	AU 9177483	A	19910417	199431	
US 5350644	A	19940927	WO 91EP734	A	19910417	199438	
			US 92941073	A	19921015		
WO 9116719	A3	19920123	WO 91EP734	A	19910417	199510	
EP 525070	B1	19951220	EP 91908382	A	19910417	199604	
			WO 91EP734	A	19910417		
DE 69115688	E	19960201	DE 615688	A	19910417	199610	
			EP 91908382	A	19910417		
			WO 91EP734	A	19910417		
JP 96015097	B2	19960214	JP 91507923	A	19910417	199611	
			WO 91EP734	A	19910417		
ES 2080313	T3	19960201	EP 91908382	A	19910417	199612	

Priority Applications (No Type Date): GB 9024831 A 19901115; GB 908512 A 19900417

Cited Patents: No.SR.Pub; 02Jnl.Ref; EP 333641; JP 57195241; US 4117210; WO 8505119; NoSR.Pub

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US 5350644	A	11	H01M-006/36	Based on patent	WO 9116719
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DE 69115688	E		H01G-009/20	Based on patent	EP 525070
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Abstract (Basic): WO 9116719 A

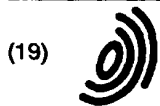
A photovoltaic cell comprises a light-transmitting electrically conductive layer deposited on a glass plate or a transparent polymer sheet to which one or more pref. porous high surface-area Ti dioxide (TiO<sub>2</sub>) layers have been applied. The last TiO<sub>2</sub> layer (and opt. also the second from last and third from last layers) is doped with a metal ion from a divalent or trivalent metal.

USE/ADVANTAGE - Provides efficient solar energy cell, having higher efficiency than Si-based solar cell, and is able to convert diffuse light more efficiently. Can be irradiated from either side or both sides. Invented cell operates as a majority carrier device so that cell voltage depends less strongly on intensity of impinging light.



Dwg.1/1  
Title Terms: EFFICIENCY; PHOTOVOLTAIC; CELL; SOLAR; ENERGY; CONVERT;  
TITANIUM; DI; OXIDE; LAYER; COATING; PHOTSENSITISER; DYE; CONTACT; REDOX  
; ELECTROLYTIC; SYSTEM  
Derwent Class: E11; E12; E23; L03; P83; P84; U12; X15  
International Patent Class (Main): H01G-009/20; H01L-031/032; H01M-006/36;  
H01M-014/00  
International Patent Class (Additional): G03C-001/64; G03C-001/725;  
G03F-007/029; H01G-009/00; H01L-031/04  
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(54) **Photoelectric conversion device and photoelectrochemical cell**

(57) A dye-sensitized photoelectric conversion device includes a conductive support, a dye-adsorbed semiconductor nanoparticulate layer, a gel electrolyte layer, and a counter electrode wherein the gel of the gel electrolyte layer contains constituent units having a carbonate group, nitrogenous heterocyclic group or quaternary ammonium salt. In another aspect, a photoelectric conversion device includes a conductive support and a photosensitive layer which contains semiconductor nanoparticulates sensitized with a specific polymethine dye.

**EP 0 911 841 A2**

## Description

[0001] This invention relates to a photoelectric conversion device, and more particularly, to a photoelectric conversion device comprising a dye-sensitized nanoparticulate semiconductor. It also relates to a photo-electrochemical cell.

## BACKGROUND OF THE INVENTION

[0002] With respect to the solar power generation, monocrystalline silicon solar batteries, polycrystalline silicon solar batteries, amorphous solar batteries, and compound solar batteries using cadmium telluride or indium copper selenide have been used in practice or become the major object of research and development. For the widespread use, problems including the manufacturing cost, the availability of source materials, and a long energy payback period must be solved. On the other hand, many solar batteries using organic materials intended for increasing the surface area and lowering the cost have also been proposed, but they have the drawbacks of low efficiency conversion and poor durability.

[0003] International Patent No. 93/20565 proposes a photoelectric conversion device using a solid electrolyte. JP-A 288142/1995, Solid State Ionics, 89 (1996), 263, and JP-A 27352/1997 propose photoelectric conversion devices using crosslinked polyethylene oxide solid polymer electrolytes for solidification. However, the photoelectric conversion devices using these solid electrolytes were found to experience a substantial decline of photoelectric conversion properties, especially short-circuiting current density and to be so tacky on their film surface that they are difficult to transport and handle during manufacture.

[0004] USP 4,927,721, 4,684,537, 5,084,365, 5,350,644, 5,463,057, 5,525,440 and JP-A 249790/1995 disclose photoelectric conversion devices using semiconductor nanoparticulates sensitized with dyes, which are often referred to as dye-sensitized photoelectric conversion devices, hereinafter, or materials and processes for preparing such converters. A first advantage of this system is that photoelectric conversion devices are obtained at a relatively low cost since inexpensive oxide semiconductors such as titanium dioxide can be used without a need for work-up to a high purity. A second advantage of this system is that photons in almost all the wavelength band of visible light can be converted into electric current since the dyes used have a broad absorption band. These features are advantageous when applied to photoelectric conversion devices for converting solar energy into electricity, that is, so-called solar batteries. Efforts have been made on the application to this field.

[0005] In order that dye-sensitized photoelectric conversion devices of this system operate at a high conversion efficiency, expensive ruthenium complex dyes must be used as the sensitizing dye, which is a potential barrier against commercial application. For this reason, there is a desire to have a photoelectric conversion device capable of high efficiency photoelectric conversion despite sensitization with inexpensive dyes such as organic dyes.

## SUMMARY OF THE INVENTION

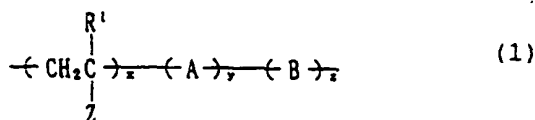
[0006] An object of the present invention is to provide a dye-sensitized photoelectric conversion device having improved photoelectric conversion efficiency and durability, and a photo-electrochemical cell using the same.

[0007] Another object of the present invention is to provide a photoelectric conversion device using an organic dye for sensitization, and a photo-electrochemical cell using the same and having improved conversion efficiency.

[0008] In a first aspect, the invention provides a photoelectric conversion device of the dye sensitization type comprising a conductive support, a layer coated on the conductive support and containing semiconductor nanoparticulates having a dye adsorbed thereto, a gel electrolyte-containing layer, and a counter electrode. The gel of the gel electrolyte-containing layer contains constituent units of at least one type having a monovalent organic residue selected from among a carbonate group, a heterocyclic group containing a nitrogen atom, and a quaternary ammonium salt.

[0009] The gel is typically a crosslinked polymer containing constituent units of at least one type having a monovalent organic residue selected from among a carbonate group, a heterocyclic group containing a nitrogen atom, and a quaternary ammonium salt. Preferably, the constituent units of the crosslinked polymer originate from an ethylenically unsaturated monomer. Further preferably, the ethylenically unsaturated monomer is at least one ethylenically unsaturated monomer having as a substituent a monovalent organic residue selected from among a carbonate group, a heterocyclic group containing a nitrogen atom, and a quaternary ammonium salt. The crosslinked polymer preferably contains, in a weight compositional ratio, 5 to 99% by weight of recurring units originating from the ethylenically unsaturated monomer.

[0010] Further preferably, the crosslinked polymer containing at least one type of recurring units originating from an ethylenically unsaturated monomer has the following formula (1):



wherein R<sup>1</sup> is hydrogen or alkyl of 1 to 4 carbon atoms, Z is a monovalent organic group containing a functional group selected from among a carbonate group, a heterocyclic group containing a nitrogen atom, and a quaternary ammonium salt, A represents recurring units derived from a compound containing an ethylenically unsaturated group, B represents recurring units derived from a compound containing at least two ethylenically unsaturated groups, letters x, y, and z represent weight compositional ratios of the recurring units associated therewith, respectively, x is from 5% to 99% by weight, y is from 0% to 70% by weight, and z is from 0.5% to 50% by weight. The ethylenically unsaturated monomer containing Z is preferably at least one member selected from among ethylene glycol carbonate methacrylate, N-vinyl pyrrolidone, N-vinyloxazolidone, and N-vinyl-N'-ethylimidazolium iodide. Preferably the crosslinked polymer accounts for a weight fraction of 2% to 80% by weight of the gel electrolyte.

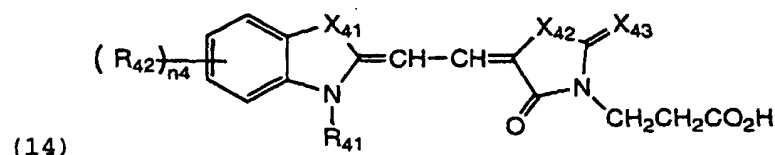
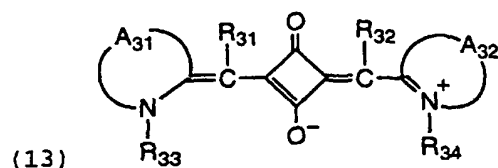
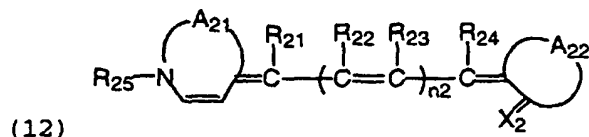
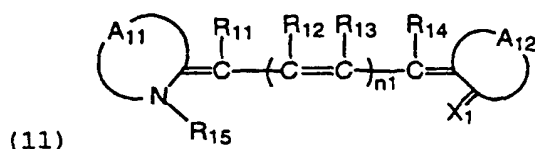
[0011] The electrolyte is typically a metal iodide, an iodine salt of a quaternary ammonium compound, a metal bromide, a bromine salt of a quaternary ammonium compound, a sulfur compound, a viologen dye, or hydroquinone-quinone. The electrolyte is preferably present in a concentration of 0.1 to 1.5 M. The electrolyte is preferably a supporting electrolyte containing an iodine salt and/or a metal iodide.

[0012] The gel electrolyte preferably contains at least one organic solvent selected from among a nitrile compound, a carbonate compound, a nitrogenous heterocyclic compound, and an ethylene glycol dialkyl ether. Further preferably, the gel electrolyte has been prepared by radical polymerization of a mixture containing a vinyl monomer, a polymerization initiator, a supporting electrolyte, and a solvent.

[0013] In the first aspect, a ruthenium complex dye or polymethine dye is typically used.

[0014] Also provided is a photo-electrochemical cell comprising the photoelectric conversion device defined above.

[0015] In a second aspect, the invention provides a photoelectric conversion device comprising at least a conductive support and a photosensitive layer. The photosensitive layer contains semiconductor nanoparticulates sensitized with a polymethine dye of the following general formula (11), (12), (13) or (14).



[0016] In formula (11),  $R_{11}$ ,  $R_{12}$ ,  $R_{13}$ , and  $R_{14}$  each are hydrogen or monovalent substituents, or  $R_{11}$  to  $R_{14}$  may bond together to form a ring,  $R_{15}$  is alkyl,  $A_{11}$  and  $A_{12}$  each are a group of atoms to form a 3 to 9-membered ring with the carbon and nitrogen atoms,  $X_1$  is oxygen or sulfur,  $n_1$  is an integer of 1 to 4, the compound of formula (11) has at least one carboxyl group as a substituent, and the compound of formula (11) may have a counter ion depending on the overall electric charge of the molecule. Preferably, the heterocycle that  $A_{11}$  forms with the carbon and nitrogen atoms is benzothiazoline, indoline, naphthothiazoline or benzindoline, and the heterocycle that  $A_{12}$  forms with the carbon atoms is rhodanine. Also preferably, the carboxyl group is attached directly or via an alkylene group to the heterocycle that  $A_{12}$  forms with the carbon atoms.

[0017] In formula (12),  $R_{21}$ ,  $R_{22}$ ,  $R_{23}$ , and  $R_{24}$  each are hydrogen or monovalent substituents, or  $R_{21}$  to  $R_{24}$  may bond together to form a ring,  $R_{25}$  is alkyl,  $A_{21}$  and  $A_{22}$  each are a group of atoms to form a 5 to 9-membered ring with the carbon and nitrogen atoms,  $X_2$  is oxygen or sulfur,  $n_2$  is an integer of 0 to 3, the compound of formula (12) has at least one carboxyl group as a substituent, and the compound of formula (12) may have a counter ion depending on the overall electric charge of the molecule. Preferably, the heterocycle that  $A_{21}$  forms with the carbon and nitrogen atoms is dihydroquinoline, and the heterocycle that  $A_{22}$  forms with the carbon atoms is rhodanine. Also preferably, the carboxyl group is attached directly or via an alkylene group to the heterocycle that  $A_{22}$  forms with the carbon atoms.

[0018] In formula (13),  $R_{31}$  and  $R_{32}$  each are hydrogen or monovalent substituents, or  $R_{31}$  and  $R_{32}$  may bond together to form a ring,  $R_{33}$  and  $R_{34}$  each are alkyl,  $A_{31}$  and  $A_{32}$  each are a group of atoms to form a 3 to 9-membered ring with the carbon and nitrogen atoms, the compound of formula (13) has at least one carboxyl group as a substituent, and the compound of formula (13) may have a counter ion depending on the overall electric charge of the molecule. Preferably, the heterocycle that  $A_{31}$  forms with the carbon and nitrogen atoms is benzothiazoline, indoline, naphthothiazoline or benzindoline, and the heterocycle that  $A_{32}$  forms with the carbon and nitrogen atoms is selected from quaternary salts of benzothiazole, indolenine, naphthothiazole and benzindolenine.

[0019] In formula (14),  $R_{41}$  is alkyl,  $R_{42}$  is a substituent,  $X_{41}$  is an alkylene group, alkylimino group, arylimino group,



oxygen atom or sulfur atom,  $X_{42}$  is an alkylimino group, arylimino group, oxygen atom or sulfur atom,  $X_{43}$  is an oxygen or sulfur atom,  $n_4$  is an integer of 0 to 4, and the compound of formula (14) may have a counter ion depending on the overall electric charge of the molecule. Preferably, both  $X_{42}$  and  $X_{43}$  are sulfur atoms.

[0020] In a further preferred embodiment, a steroid compound having a carboxyl group is adsorbed to the semiconductor nanoparticulates along with the polymethine dye.

[0021] Also a photo-electrochemical cell is provided comprising the photoelectric conversion device according to the second aspect, an electric charge transfer layer and a counter electrode.

#### BRIEF DESCRIPTION OF THE DRAWINGS

[0022]

FIG. 1 is a diagrammatic sectional view showing the layer structure of a photo-electrochemical cell according to the first embodiment.

FIG. 2 is a diagrammatic sectional view showing the layer structure of a photo-electrochemical cell according to the second embodiment.

FIG. 3 is a diagrammatic sectional view showing the layer structure of a modified photo-electrochemical cell according to the second embodiment.

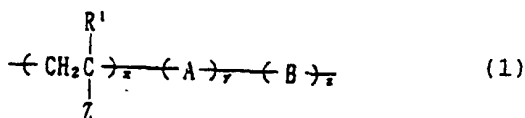
#### BEST MODE FOR CARRYING OUT THE INVENTION

##### First embodiment

[0023] The gel of the gel electrolyte-containing layer in the photoelectric conversion device according to the invention contains constituent units of at least one type having a monovalent organic residue selected from among a carbonate group, a heterocyclic group containing a nitrogen atom, and a quaternary ammonium salt. The gel is preferably a crosslinked polymer.

[0024] Typically, the constituent units of the crosslinked polymer originate from an ethylenically unsaturated monomer, which is preferably at least one ethylenically unsaturated monomer having as a substituent a monovalent organic residue selected from among a carbonate group, a heterocyclic group containing a nitrogen atom, and a quaternary ammonium salt. Further preferably, the crosslinked polymer contains, in a weight compositional ratio, 5 to 99% by weight of recurring units originating from the ethylenically unsaturated monomer having the above-described substituent.

[0025] Preferably, the crosslinked polymer containing at least one type of recurring units originating from an ethylenically unsaturated monomer has the following formula (1):



wherein  $R^1$  is hydrogen or alkyl of 1 to 4 carbon atoms, Z is a monovalent organic group containing a functional group selected from among a carbonate group, a heterocyclic group containing a nitrogen atom, and a quaternary ammonium salt, A represents recurring units derived from a compound containing an ethylenically unsaturated group, B represents recurring units derived from a compound containing at least two ethylenically unsaturated groups, letters x, y, and z represent weight compositional ratios of the recurring units associated therewith, respectively, x is from 5% to 99% by weight, y is from 0% to 70% by weight, and z is from 0.5% to 50% by weight.

[0026] According to the invention, the dye-sensitized photoelectric conversion device is defined as comprising a conductive support, a layer coated on the conductive support and containing semiconductor nanoparticulates having a dye adsorbed thereto, which is also referred to as a photosensitive layer, a gel electrolyte-containing layer, and a counter electrode.

[0027] The conductive supports may be metal supports which themselves are electrically conductive or supports of glass or plastics having a conductive agent layer on their surface. In the latter case, the preferred conductive agents are metals such as platinum, gold, silver, copper, aluminum, rhodium, and indium, carbon, and conductive metal oxides such as indium-tin compound oxide and tin oxide doped with fluorine. Especially preferred is a conductive glass support in the form of a transparent support of soda lime float glass having deposited thereon a conductive layer of fluorine-doped tin dioxide. The conductive agent layer is preferably about 0.02  $\mu\text{m}$  to about 10  $\mu\text{m}$  thick.

[0028] It is recommended that the conductive supports have a lower surface resistivity. The preferred range of surface resistivity is up to  $100 \Omega/\text{cm}^2$ , more preferably up to  $40 \Omega/\text{cm}^2$ .

[0029] It is also recommended that the conductive supports be substantially transparent. The term "substantially transparent" means that the light transmittance of the support is at least 10%, preferably at least 50%, more preferably at least 70%. As the transparent conductive support, glass or plastic supports having conductive metal oxide coated thereon are preferable. The coverage or weight of conductive metal oxide coated is preferably 0.1 to 100 g per square meter of the glass or plastic support. Where transparent conductive supports are used, it is desired that light enters the device from the support side.

[0030] In the photosensitive layer, nanoparticulates of metal chalcogenides (e.g., oxides, sulfides and selenides) or perovskite may be used as the nanoparticulate semiconductor. Examples of the metal chalcogenides include oxides of titanium, tin, zinc, tungsten, zirconium, hafnium, strontium, indium, cerium, yttrium, lanthanum, vanadium, niobium, and tantalum, cadmium sulfide, and cadmium selenide. Examples of the perovskite are strontium titanate and calcium titanate. Of these, titanium oxide, zinc oxide, tin oxide and tungsten oxide are especially preferred.

[0031] The semiconductor nanoparticulates preferably have a mean particle size of 5 to 200 nm, more preferably 8 to 100 nm, expressed by the diameter of a circle of equivalent area to the projected area of a primary particle.

[0032] Various methods are employable for coating semiconductor nanoparticulates to a conductive support. Exemplary methods are a method of applying a dispersion liquid or colloid solution of semiconductor nanoparticulates onto a conductive support, and a method of applying a semiconductor nanoparticulate precursor onto a conductive support and allowing the precursor to be hydrolyzed with moisture in air, thereby forming a semiconductor nanoparticulate coating. The dispersion liquid of semiconductor nanoparticulates can be prepared by such methods as grinding in a mortar, milling and dispersing in a mill, and synthesizing a semiconductor under such conditions that the semiconductor may precipitate in a solvent as nanoparticulates. The dispersing media may be water or various organic solvents such as methanol, ethanol, dichloromethane, acetone, acetonitrile, and ethyl acetate. In forming a dispersion, polymers, surfactants, acids or chelates may be used as the dispersant if necessary.

[0033] Semiconductor nanoparticulates are desired to have a greater surface area so that more dye may be adsorbed thereon. The semiconductor nanoparticulate layer as applied onto the support should preferably have a surface area which is greater than the projected area by a factor of at least 10, more preferably at least 100. No upper limit is imposed on the surface area although the upper limit is usually a multiplication factor of about 1,000.

[0034] In general, as the semiconductor nanoparticulate layer becomes thicker, the amount of the dye carried per unit projected area increases so that the capture rate of light becomes higher, but the loss by charge recombination becomes greater because the diffusion distance of generated electrons increases. For this reason, the semiconductor nanoparticulate layer has an appropriate range of thickness which is typically 0.1 to 100  $\mu\text{m}$ . When the semiconductor nanoparticulate layer is used in a photo-electrochemical cell, an appropriate thickness is 1 to 30  $\mu\text{m}$ , especially 3 to 20  $\mu\text{m}$ . After coating on a support, semiconductor nanoparticulates may be fired in order to bring the particulates into electronic contact and improve the strength and the adhesion to the support of the coating. The preferred range of firing temperature is from 40°C to less than 700°C. Further, after firing, the semiconductor nanoparticulates may be subject to chemical plating in an aqueous solution of titanium tetrachloride or electrochemical plating in an aqueous solution of titanium trichloride, for the purpose of increasing the surface area of semiconductor nanoparticulates or increasing the purity in the vicinity of semiconductor nanoparticulates for increasing the efficiency of electron injection from the dye into the semiconductor nanoparticulates.

[0035] The coverage or weight of semiconductor nanoparticulates coated is preferably 0.5 to 500 g, more preferably 5 to 100 g per square meter of the support.

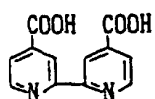
[0036] The dyes, also called chromophores or sensitizers, which are used in the present invention are preferably ruthenium complex dyes and/or polymethine dyes. Further preferably, the dyes have appropriate interlocking groups to surfaces of semiconductor nanoparticulates. Preferred interlocking groups include cyano, and  $\text{PO}_3\text{H}_2$  groups, as well as chelating groups having  $\pi$ -conducting character such as oximes, dioximes, hydroxyquinolines, and alpha-keto enolates. Of these,  $\text{PO}_3\text{H}_2$  groups are especially preferred.

[0037] Where ruthenium complex dyes are used in the practice of the invention, they are preferably of the following general formula (2).

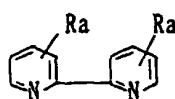


In formula (2), Ru is ruthenium, X is a ligand selected from the group consisting of Cl, SCN,  $\text{H}_2\text{O}$ , Br, I, CN, -NCO, and SeCN, letter n is equal to 1 or 2, preferably equal to 2, L and  $\text{L}_a$  each are an organic ligand selected from the following ligands L-1 to L-8.

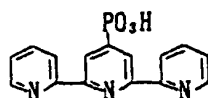
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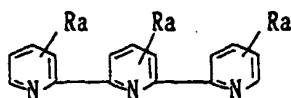
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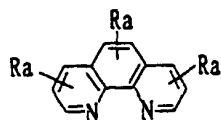
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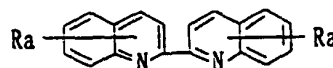
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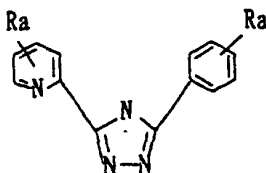
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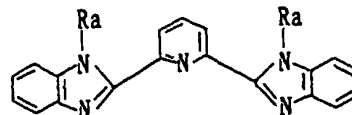
L-6



L-7



L-8



[0038] In the formulae, Ra is hydrogen, a halogen atom or a substituted or unsubstituted alkyl, aralkyl or aryl group having 1 to 12 carbon atoms.

[0039] The ruthenium complex dyes which can be used herein are, for example, the complex dyes described in USP 4,927,721, 4,684,537, 5,084,365, 5,350,644, 5,463,057, 5,525,440 and JP-A 249790/1995.

[0040] Preferred illustrative, non-limiting, examples of the ruthenium complex dyes which can be used herein are given below.

Table 1

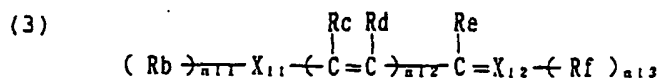
No.	X	n	L	La
R-1	SCN	2	L-1	L-1
R-2	CN	2	L-1	L-1
R-3	Cl	2	L-1	L-1

EP 0 911 841 A2

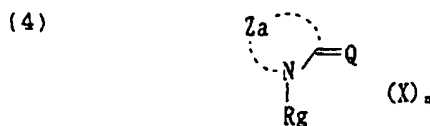
Tabl 1 (continued)

No.	X	n	L	La
R-4	Br	2	L-1	L-1
R-5	I	2	L-1	L-1
R-6	SCN	2	L-1	L-2
R-7	SCN	1	L-1	L-3
R-8	Cl	1	L-1	L-4
R-9	I	2	L-1	L-5
R-10	SCN	2	L-1	L-6
R-11	CN	2	L-1	L-7
R-12	Cl	1	L-1	L-8

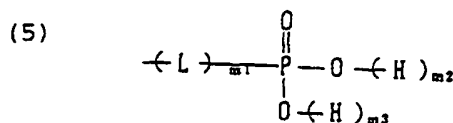
[0041] Where polymethine dyes are used in the practice of the invention, they are preferably of the following general formula (3) or (4).



[0042] In formula (3), Rb and Rf are hydrogen, alkyl groups, aryl groups or heterocyclic residues, Rc to Re are hydrogen or substituents. Alternatively, Rb to Rf, taken together, may form a ring.  $X_{11}$  and  $X_{12}$  are nitrogen, oxygen, sulfur, selenium or tellurium. Letters  $n_{11}$  and  $n_{13}$  are integers of 0 to 2, and  $n_{12}$  is an integer of 1 to 6. The compound of formula (3) may have a counter ion if necessary from the overall electric charge of its molecule.



[0043] In formula (4), Za is a group of non-metallic atoms necessary to form a nitrogenous heterocycle. Rg is an alkyl or aryl group. Q is a methine or polymethine group necessary for the compound of formula (4) to become a methine dye. It is noted that Za, Rg and Q represent groups which enable the compound of formula (4) to have at least one substituent of the general formula (5). X is a charge equilibrating counter ion. Letter n is a number of 0 to 10 necessary to neutralize the electric charge of the molecule.



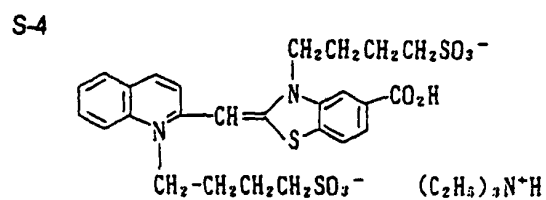
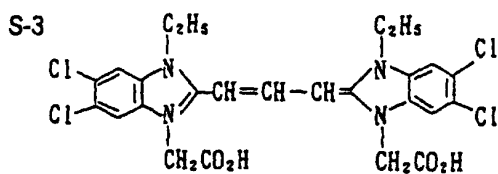
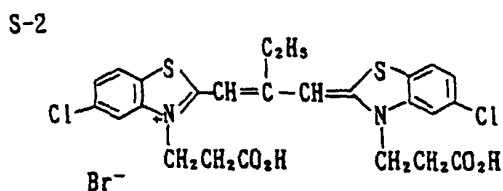
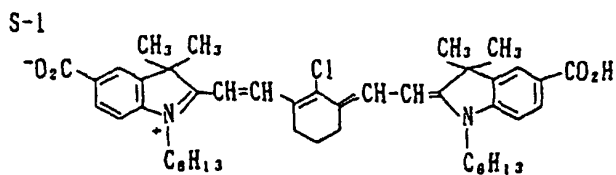
[0044] In formula (5), L is an oxygen atom, sulfur atom or amino group, letter  $m_1$  is equal to 0 or 1,  $m_2$  and  $m_3$  each are equal to 0 or 1. Where  $m_2$  or  $m_3$  is 0, the substituent of formula (5) has a negative charge.

[0045] Illustrative examples of the polymethine dye are described in M. Okawara, T. Kitao, T. Hirasima & M. Matuoka, "Organic Colorants" (Elsevier).

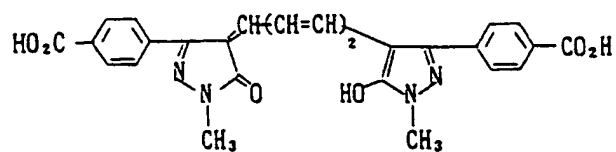
EP 0 911 841 A2

[0046] Preferred, illustrative, non-limiting examples of the polymethine dyes of general formulae (3) and (4) are given below.

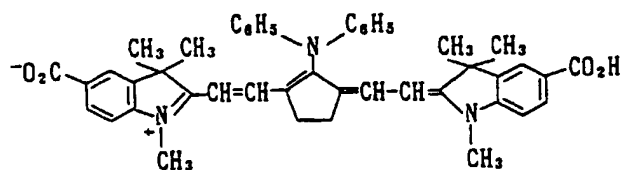
[0047] Examples of the dye of formula (3):



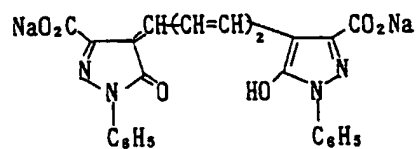
S-5



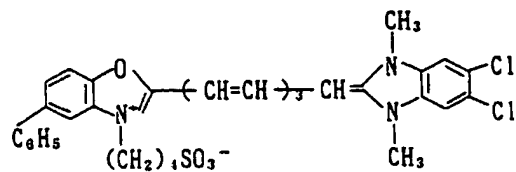
S-6



S-7



S-8

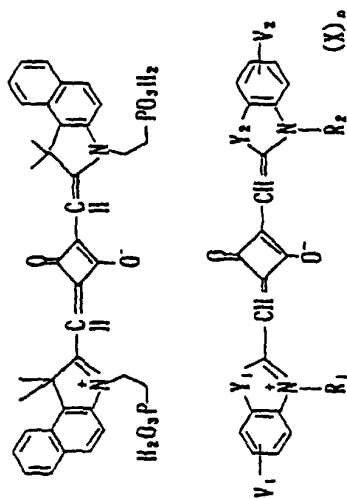


45 [0048] Examples of the dye of formula (4):

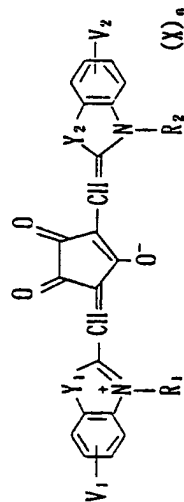
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S-9

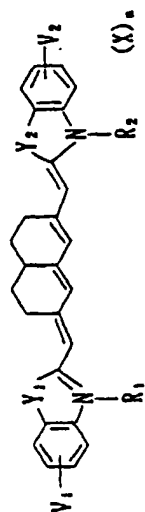


Compound	Y <sub>1</sub>	Y <sub>2</sub>	V <sub>1</sub>	V <sub>2</sub>	R <sub>1</sub>	R <sub>2</sub>	X	n
S-10	S	S	5-PO(OH) <sub>2</sub>	5-PO(OH) <sub>2</sub>	C <sub>2</sub> H <sub>5</sub>	C <sub>2</sub> H <sub>5</sub>	-	-
S-11	S	S	6-PO(OH) <sub>2</sub>	6-PO(OH) <sub>2</sub>	C <sub>2</sub> H <sub>5</sub>	C <sub>2</sub> H <sub>5</sub>	-	-
S-12	S	S	5-PO(OH) <sub>2</sub>	5-PO(OH) <sub>2</sub>	-(CH <sub>2</sub> ) <sub>3</sub> SO <sub>3</sub> <sup>-</sup>	-(CH <sub>2</sub> ) <sub>3</sub> SO <sub>3</sub> <sup>-</sup>	Na <sup>+</sup>	2
S-13	O	O	6-PO(OH) <sub>2</sub>	6-PO(OH) <sub>2</sub>	CH <sub>3</sub>	CH <sub>3</sub>	-	-
S-14	C(Me) <sub>2</sub>	C(Me) <sub>2</sub>	6-PO(OH) <sub>2</sub>	6-PO(OH) <sub>2</sub>	C <sub>2</sub> H <sub>5</sub>	C <sub>2</sub> H <sub>5</sub>	-	-

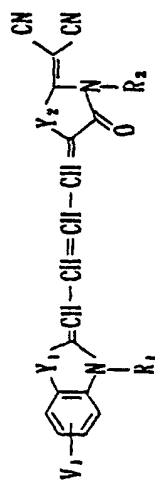



Compound	Y <sub>1</sub>	Y <sub>2</sub>	V <sub>1</sub>	V <sub>2</sub>	R <sub>1</sub>	R <sub>2</sub>	X	n
S-15	S	S	5-PO(OH) <sub>2</sub>	5-PO(OH) <sub>2</sub>	C <sub>2</sub> H <sub>5</sub>	C <sub>2</sub> H <sub>5</sub>	-	1
S-16	C(Me) <sub>2</sub>	C(Me) <sub>2</sub>	6-PO(OH) <sub>2</sub>	6-PO(OH) <sub>2</sub>	C <sub>2</sub> H <sub>5</sub>	C <sub>2</sub> H <sub>5</sub>	-	1





Compound	Y <sub>1</sub>	Y <sub>2</sub>	V <sub>1</sub>	V <sub>2</sub>	R <sub>1</sub>	R <sub>2</sub>	X	n
S-17	S	S	5-PO(OH) <sub>2</sub>	5-PO(OH) <sub>2</sub>	ClH <sub>5</sub>	ClH <sub>5</sub>	I <sup>-</sup>	1
S-18	S	S	5-PO-O- OH	5-PO(OH) <sub>2</sub>	C <sub>2</sub> H <sub>5</sub>	C <sub>2</sub> H <sub>5</sub>	-	-



Compound	Y <sub>1</sub>	Y <sub>2</sub>	V <sub>1</sub>	R <sub>1</sub>	R <sub>2</sub>
S-19	S	S	5-PO(OH) <sub>2</sub>	C <sub>2</sub> H <sub>5</sub>	ClH <sub>2</sub>
S-20	S	S	5-PO(OH) <sub>2</sub>	ClH <sub>2</sub>	

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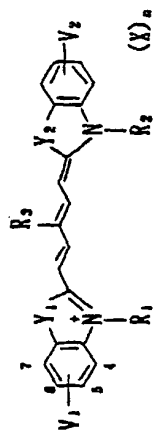
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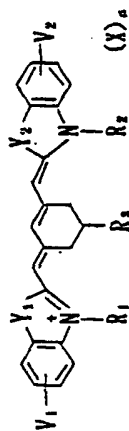
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Compound	Y <sub>1</sub>	Y <sub>2</sub>	V <sub>1</sub>	V <sub>2</sub>	R <sub>1</sub>	R <sub>2</sub>	R <sub>3</sub>	X	n
S-21	S	S	5-PO(OH) <sub>2</sub>	5, 6-di-Cl <sub>2</sub>	Cl <sub>2</sub>	C <sub>2</sub> H <sub>5</sub>	Cl <sub>2</sub>	I <sup>-</sup>	1
S-22	S	S	5-PO(OH) <sub>2</sub>	5-PO(OH) O	Cl <sub>2</sub>	Cl <sub>2</sub>	Cl <sub>2</sub>	-	-

Compound	$Y_1$	$Y_2$	$V_1$	$V_2$	$R_1$	$R_2$	$R_3$	X	n
S-23	S	S	$PO(OH)_2$	$PO(OH)_2$	$CH_3$	$CH_3$	$CH_3$	$I^-$	1
S-24	S	S	$OP(O)(OH)_2$	$OP(O)(OH)_2$	$C_2H_5$	$C_2H_5$	$C_2H_5$	$Cl^-$	-



[0049] The compounds of general formulae (3) and (4) can be synthesized by the methods described in F.M. Harmer, Heterocyclic Compounds - Cyanine Dyes and Related Compounds, John Wiley & Sons, New York, London, 1964; D.M. Sturmer, Heterocyclic Compounds - Special topics in heterocyclic chemistry," Chap. 18, Sec. 14, pp. 482-515, John Wiley & Sons, New York, London, 1977; Rodd's Chemistry of Carbon Compounds, 2nd Ed., vol. IV, part B, 1977, Chap. 15, pp. 369-422, Elsevier Science Publishing Company Inc., New York; and British Patent No. 1,077,611.

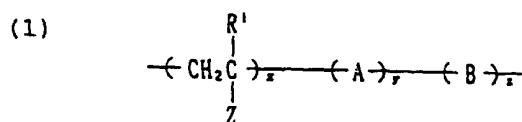
[0050] The dye is adsorbed to semiconductor nanoparticulates, most often by immersing fully dry semiconductor nanoparticulates in a dye solution for several hours. The dye adsorption may be done at room temperature or by heating under reflux as described in JP-A 249790/1995. The dye adsorption may be done either prior to or subsequent to the coating of semiconductor nanoparticulates. It is also acceptable that semiconductor nanoparticulates and the dye are simultaneously coated whereupon adsorption takes place. It is desirable to remove the unadsorbed dye by washing.

Where the coated film is fired, it is preferred that the dye adsorption be done subsequent to firing. It is especially preferred that the dye is quickly adsorbed to the coated film after firing and before water adsorbs to the surface of the coated film. For adsorption, a single dye or a mixture of dyes may be used. For the application to photo-electrochemical cells, dyes are selected and mixed so as to make the wavelength range of photoelectric conversion as broad as possible.

[0051] Also for the purpose of reducing the association or interaction between dyes, a colorless compound may be co-adsorbed. Hydrophobic compounds to be co-adsorbed are steroid compounds having a carboxyl group, e.g., cholic acid.

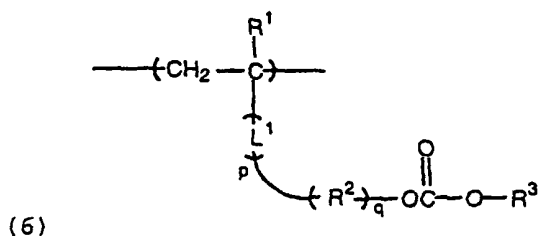
[0052] After the adsorption of the dye, the semiconductor nanoparticulates may be surface treated with amines. Preferred amines are pyridine, 4-tert-butylpyridine and polyvinylpyridine. The amines may be used as such if they are liquid or as solutions in organic solvents.

[0053] The gel used herein designates a state that colloid particles or polymeric solutes have lost independent mobility due to their interaction, coalesced to have a structure and solidified. The gel electrolytes including crosslinked polymers used in the invention are now described in detail. The gel electrolyte of the invention is represented by formula (1).



[0054] Herein  $R^1$  is hydrogen or alkyl of 1 to 4 carbon atoms. Preferably,  $R^1$  is hydrogen or methyl.

[0055] Z is a monovalent organic group containing a functional group selected from among a carbonate group, a heterocyclic group containing a nitrogen atom, and a quaternary ammonium salt. Preferably the organic groups represented by Z have 2 to 20 carbon atoms. Where Z contains a carbonate group, the preferred recurring units have the structure of the following formula (6).



[0056] Herein  $R^1$  is hydrogen or alkyl of 1 to 4 carbon atoms. Preferably,  $R^1$  is hydrogen or methyl.  $L^1$  represents COO, OCO, CONR<sup>4</sup>, NR<sup>5</sup>CO or phenylene groups wherein  $R^4$  and  $R^5$  each are hydrogen or alkyl of 1 to 4 carbon atoms and preferably, hydrogen or methyl.  $R^2$  is alkylene of 1 to 12 carbon atoms.  $R^3$  is hydrogen or alkyl of 1 to 4 carbon atoms.  $R^3$  may form a ring with  $R^2$ . Letters p and q each are equal to 0 or 1.

[0057] Where Z contains a heterocycle having a nitrogen atom, the heterocycle is preferably selected from pyrrolidone, imidazole, pyridine, morpholine, piperidine, succinimide, oxazolidone, and 5-methyloxazolidone. In this case, the ethylenically unsaturated group may be attached to the nitrogen atom in the heterocycle directly or via a linking group to constitute the recurring units.

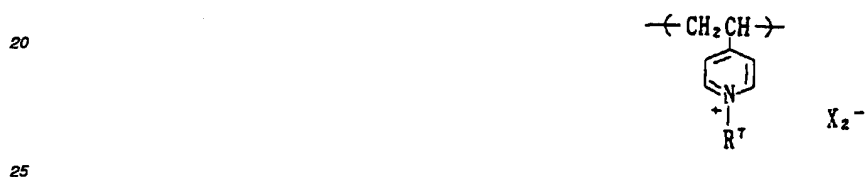
[0058] Where Z is selected from quaternary ammonium salts, the preferred recurring units have the structure of the following general formula (7), (8), (9) or (10).

General formula (7):



[0059] Herein,  $\text{R}^6$  represents substituted or unsubstituted alkyl, aralkyl, alkenyl and alkynyl groups having 1 to 20 carbon atoms. Preferably  $\text{R}^6$  represents normal or branched alkyl or aralkyl groups having 1 to 12 carbon atoms.  $\text{X}_1^-$  is a halide ion such as  $\text{Cl}^-$ ,  $\text{Br}^-$  or  $\text{I}^-$ , and preferably  $\text{I}^-$ .

General formula (8):



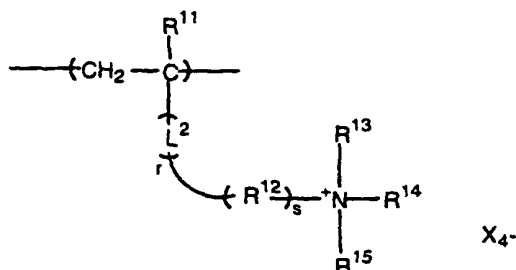
[0060] Herein,  $\text{R}^7$  represents substituted or unsubstituted alkyl, aralkyl, alkenyl and alkynyl groups having 1 to 20 carbon atoms. Preferably  $\text{R}^7$  represents normal or branched alkyl or aralkyl groups having 1 to 12 carbon atoms.  $\text{X}_2^-$  is a halide ion such as  $\text{Cl}^-$ ,  $\text{Br}^-$  or  $\text{I}^-$ , and preferably  $\text{I}^-$ .

General formula (9):



[0061] Herein,  $\text{R}^8$ ,  $\text{R}^9$ , and  $\text{R}^{10}$  represent substituted or unsubstituted alkyl, aralkyl, alkenyl and alkynyl groups having 1 to 20 carbon atoms.  $\text{R}^8$ ,  $\text{R}^9$ , and  $\text{R}^{10}$  may be the same or different, and may form a ring together. Preferably the groups represented by  $\text{R}^8$ ,  $\text{R}^9$ , and  $\text{R}^{10}$  have 1 to 12 carbon atoms.  $\text{X}_3^-$  is a halide ion such as  $\text{Cl}^-$ ,  $\text{Br}^-$  or  $\text{I}^-$ , and preferably  $\text{I}^-$ .

General formula (10):



[0062] Herein,  $\text{R}^{11}$  represents hydrogen or alkyl of 1 to 4 carbon atoms. Preferably  $\text{R}^{11}$  represents hydrogen or methyl.  $\text{L}^2$  represents  $\text{COO}$ ,  $\text{OCO}$ ,  $\text{CONR}^{16}$ ,  $\text{NR}^{17}\text{CO}$  or phenylene groups wherein  $\text{R}^{16}$  and  $\text{R}^{17}$  each are hydrogen or alkyl of 1 to 4 carbon atoms.  $\text{R}^{12}$  is alkylene of 1 to 12 carbon atoms.  $\text{R}^{13}$ ,  $\text{R}^{14}$ , and  $\text{R}^{15}$  represent substituted or unsubstituted alkyl, aralkyl, alkenyl and alkynyl groups having 1 to 20 carbon atoms.  $\text{R}^{13}$ ,  $\text{R}^{14}$ , and  $\text{R}^{15}$  may be the same or different, and may form a ring together. Preferably the groups represented by  $\text{R}^{13}$ ,  $\text{R}^{14}$ , and  $\text{R}^{15}$  have 1 to 12 carbon atoms.  $\text{X}_4^-$  is a halide ion such as  $\text{Cl}^-$ ,  $\text{Br}^-$  or  $\text{I}^-$ , and preferably  $\text{I}^-$ . Letters  $r$  and  $s$  each are equal to 0 or 1.

[0063] The weight compositional ratio  $x$  that the recurring units containing  $Z$  account for in the crosslinked polymer is preferably from 5% to 99% by weight, more preferably 20% to 95% by weight. The recurring units containing  $Z$  may be a combination of recurring units containing a carbonate group, recurring units containing a nitrogenous heterocycle, and recurring units containing a quaternary ammonium salt.

[0064] Referring back to formula (1),  $A$  represents recurring units derived from a compound containing an ethylenically unsaturated group. Preferred examples of the compound containing an ethylenically unsaturated group from which recurring units represented by  $A$  are derived include

esters and amides derived from acrylic acid or  $\alpha$ -alkylacrylic acids (e.g., methacrylic acid), for example, N-i-propylacrylamide, N-n-butylacrylamide, N-t-butylacrylamide, N,N-dimethylacrylamide, N-methylmethacrylamide, acrylamide, 2-acrylamide-2-methylpropanesulfonic acid, methacrylamide, diacetone acrylamide, N-methylol acrylamide, N-methylol methacrylamide, methyl acrylate, ethyl acrylate, hydroxyethyl acrylate, n-propyl acrylate, i-propyl acrylate, 2-hydroxypropyl acrylate, 2-methyl-2-nitropropyl acrylate, n-butyl acrylate, i-butyl acrylate, t-butyl acrylate, t-pentyl acrylate, 2-methoxyethyl acrylate, 2-ethoxyethyl acrylate, 2-methoxymethoxyethyl acrylate, 2,2,2-trifluoroethyl acrylate, 2,2-dimethylbutyl acrylate, 3-methoxybutyl acrylate, ethylcarbitol acrylate, phenoxyethyl acrylate, n-pentyl acrylate, 3-pentyl acrylate, octafluoropentyl acrylate, n-hexyl acrylate, cyclohexyl acrylate, cyclopentyl acrylate, cetyl acrylate, benzyl acrylate, n-octyl acrylate, 2-ethylhexyl acrylate, 4-methyl-2-propylpentyl acrylate, heptadecafluorodecyl acrylate, n-octadecyl acrylate, methyl methacrylate, 2,2,2-trifluoroethylethyl methacrylate, tetrafluoropropyl methacrylate, hexafluoropropyl methacrylate, hydroxyethyl methacrylate, 2-hydroxypropyl methacrylate, i-butyl methacrylate, sec-butyl methacrylate, n-octyl methacrylate, 2-methoxyethyl methacrylate, 2-ethoxyethyl methacrylate, benzyl methacrylate, heptadecafluorodecyl methacrylate, n-octadecyl methacrylate, 2-isobornyl methacrylate, 2-norbornylmethyl methacrylate, 5-norbornene-2-ylmethyl methacrylate, 3-methyl-2-norbornylmethyl methacrylate, and dimethylaminoethyl methacrylate;

acrylic acid or  $\alpha$ -alkylacrylic acids (e.g., acrylic acid, methacrylic acid, and itaconic acid); vinyl esters (e.g., vinyl acetate); esters derived from maleic acid or fumaric acid (e.g., dimethyl maleate, dibutyl maleate, and diethyl fumarate); sodium salts of maleic acid, fumaric acid, and p-styrenesulfonic acid; acrylonitrile, methacrylonitrile, dienes (e.g., butadiene, cyclopentadiene, and isoprene), aromatic vinyl compounds (e.g., styrene, p-chlorostyrene, t-butylstyrene,  $\alpha$ -methylstyrene, and sodium styrenesulfonate), N-vinylformamide, N-vinyl-N-methylformamide, N-vinylacetamide, N-vinyl-N-methylacetamide, vinylsulfonic acid, sodium vinylsulfonate, sodium allylsulfonate, sodium methallylsulfonate, vinylidene fluoride, vinylidene chloride, vinyl alkyl ethers (e.g., methyl vinyl ether), ethylene, propylene, 1-butene, isobutene, and N-phenylmaleimide.

[0065] These compounds having an ethylenically unsaturated group may be used in combination. Other compounds having an ethylenically unsaturated group are described in *Research Disclosure*, No. 1955 (July 1980). The weight compositional ratio  $y$  that the recurring units represented by  $A$  (derived from the compound having an ethylenically

unsaturated group) account for in the crosslinked polymer is preferably from 0% to 70% by weight, more preferably 0% to 50% by weight.

[0066] In formula (1), B represents recurring units derived from a compound containing at least two ethylenically unsaturated groups. Examples of the compound containing at least two ethylenically unsaturated groups include divinyl benzene, 4,4'-isopropylidene diphenylene diacrylate, 1,3-butylene diacrylate, 1,3-butylene dimethacrylate, 1,4-cyclohexylene dimethylene dimethacrylate, diethylene glycol dimethacrylate, diisopropylidene glycol dimethacrylate, divinylloxymethane, ethylene glycol diacrylate, ethylene glycol dimethacrylate, diethylene glycol diacrylate, diethylene glycol dimethacrylate, ethylidene diacrylate, ethylidene dimethacrylate, allyl acrylate, allyl methacrylate, 1,6-diacrylamidehexane, N,N'-methylene bisacrylamide, N,N'-(1,2-dihydroxy)ethylene bisacrylamide, 2,2-dimethyl-1,3-trimethylene dimethacrylate, phenylethylene dimethacrylate, tetraethylene glycol dimethacrylate, tetramethylene diacrylate, tetramethylene dimethacrylate, 2,2,2-trichloroethylidene dimethacrylate, triethylene glycol diacrylate, pentaerythritol triacrylate, trimethylol propane triacrylate, tetramethylolmethane tetracrylate, triethylene glycol dimethacrylate, 1,3,5-triacryloylhexahydro-s-triazine, bisacrylamidoacetic acid, ethylidyne trimethacrylate, propylidyne triacrylate, and vinyl allyloxyacetate. Inter alia, divinyl benzene, ethylene glycol dimethacrylate, ethylene glycol diacrylate, ethylene glycol dimethacrylate, diethylene glycol diacrylate, diethylene glycol dimethacrylate, triethylene glycol diacrylate, and triethylene glycol dimethacrylate are preferred. The weight compositional ratio z that the recurring units represented by B (derived from the compound having ethylenically unsaturated groups) account for in the crosslinked polymer is preferably from 0.5% to 50% by weight, more preferably 1.0% to 30% by weight.

[0067] Preferably, the crosslinked polymer accounts for a weight fraction of 2.0% to 80% by weight, more preferably 3.0% to 60% by weight of the gel electrolyte according to the invention.

[0068] Preferred, non-limiting, examples of the crosslinked polymer constituting the gel electrolyte according to the invention are given below. In the following formulas, x, y and other suffixes represent weight compositional ratios.

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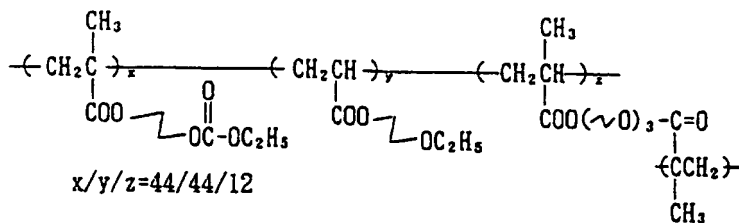
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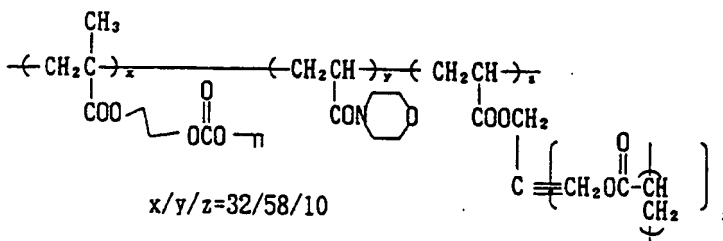


$$x/y = 93/7$$

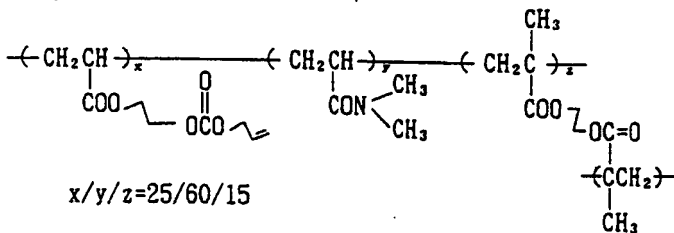
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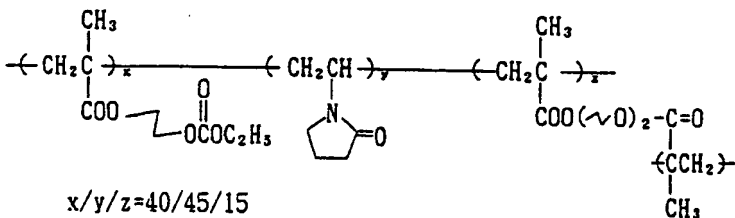
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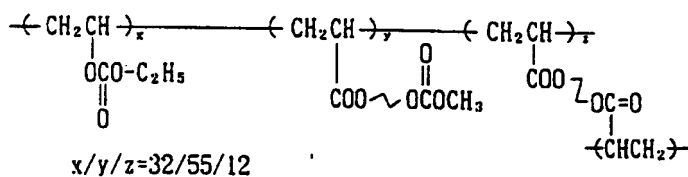
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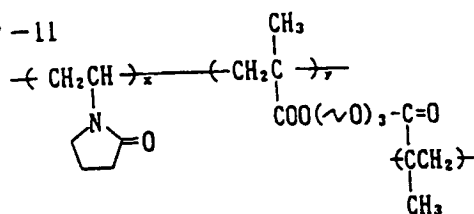
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P - 10

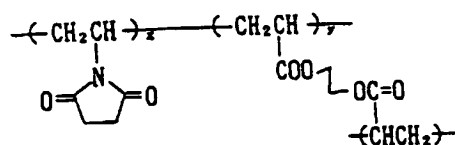


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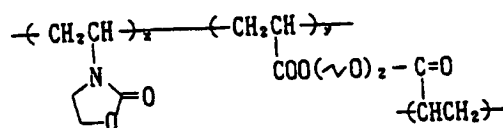
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P-12



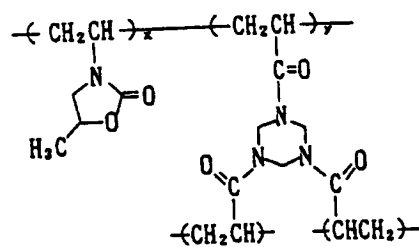
x/y=80/20

P-13



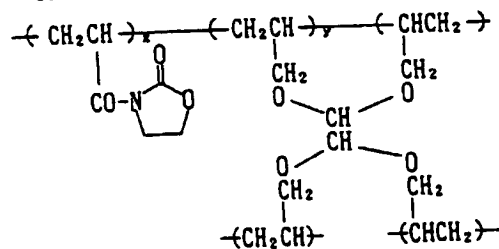
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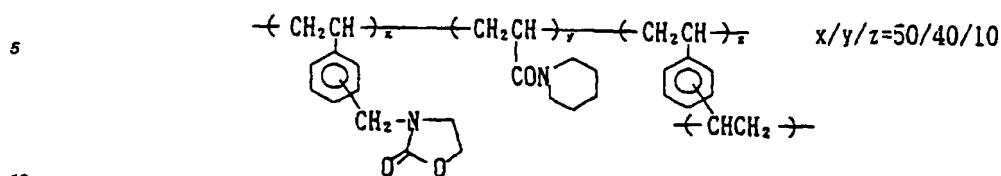
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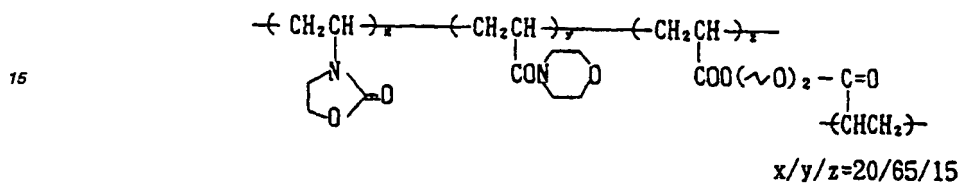


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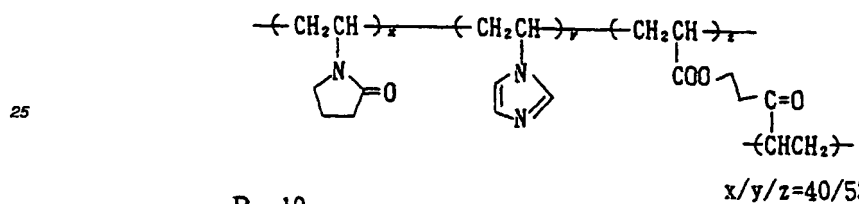
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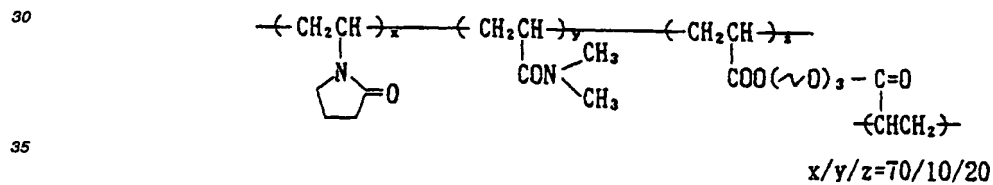
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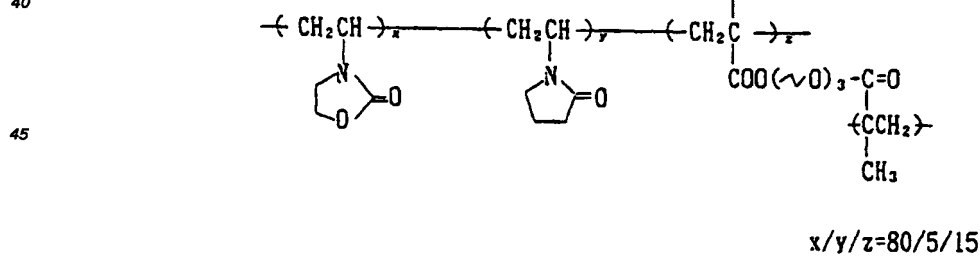
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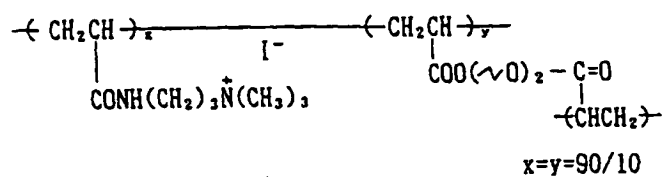
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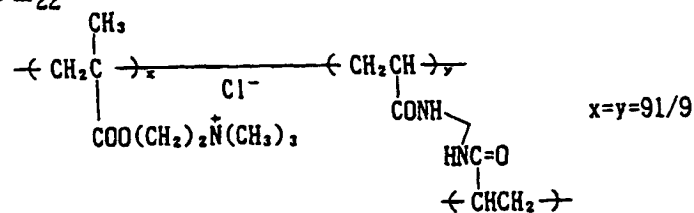
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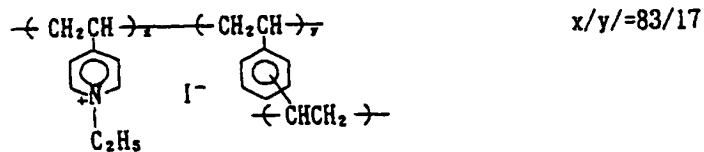
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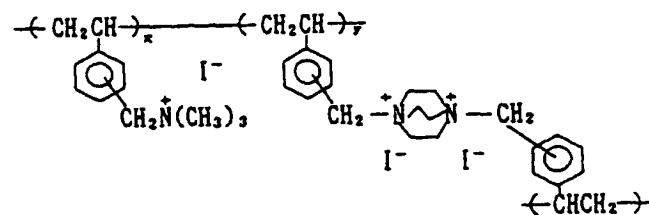
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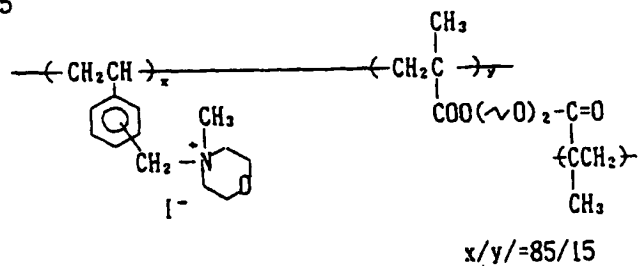
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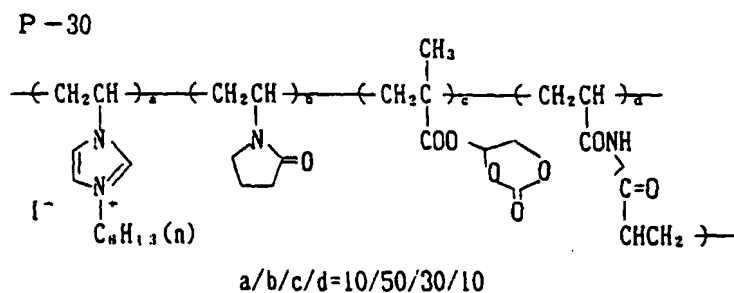
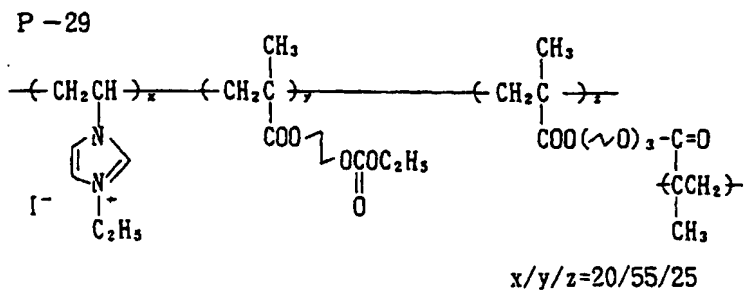
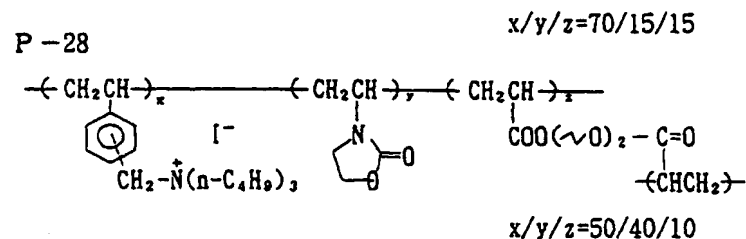
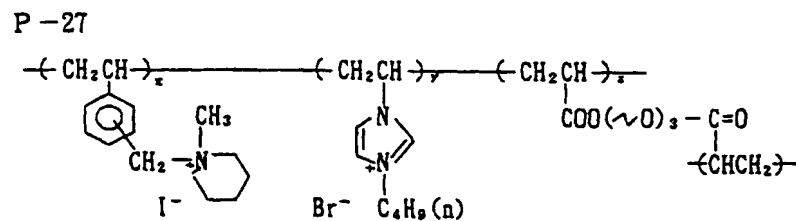
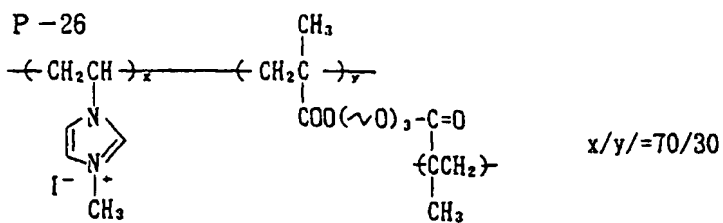


P-24



P-25





[0069] The crosslinked polymers used herein can be synthesized by radical polymerization which is one of ordinary polymer synthesis processes as described in T. Ohtsu and M. Kinoshita, "Experiments of Polymer Synthesis," Kagaku

Dojin K.K., 1972, and T. Ohtsu, "Polymerization Reaction Theory 1, Radical Polymerization (I)," Kagaku Dojin K.K. The crosslinked polymers used herein can also be synthesized by radical polymerization assisted by thermal, optical, electron beam or electrochemical means, especially thermally assisted radical polymerization. When the crosslinked polymers used herein are formed by thermally assisted radical polymerization, there are used polymerization initiators, examples of which include azo initiators such as 2,2'-azobisisobutyronitrile, 2,2'-azobis(2,4-dimethylvaleronitrile), and dimethyl-2,2'-azobis(2-methylpropionate)(dimethyl-2,2'-azobisisobutyrate), and peroxide initiators such as lauryl peroxide, benzoyl peroxide, and tert-butyl peroctoate. The polymerization initiator is preferably added in an amount of 0.01 to 20% by weight, more preferably 0.1 to 10% by weight of the total weight of monomers.

[0070] Typically, the gel electrolyte according to the invention is constructed by the crosslinked polymer, an electrolyte and a solvent. The latter two are now described.

[0071] The electrolytes used herein include metal iodides such as LiI, NaI, KI, CsI, and  $\text{CaI}_2$ ; iodine salts of quaternary ammonium compounds such as tetraalkylammonium iodide and pyridinium iodide;  $\text{Br}_2$  and metal bromides such as LiBr, NaBr, KBr, CsBr, and  $\text{CaBr}_2$ ;  $\text{Br}_2$  and bromine salts of quaternary ammonium compounds such as tetraalkyl ammonium bromides and pyridinium bromide; metal complexes such as ferrocyanate-ferricyanate salts and ferrocene-ferricinium ions; sulfur compounds such as sodium polysulfide and alkylthiol-alkyldisulfides; viologen dyes, and hydroquinone-quinone. Of these, metal iodides such as LiI, NaI, KI, CsI, and  $\text{CaI}_2$ , and iodine salts of quaternary ammonium compounds such as tetraalkylammonium iodide and pyridinium iodide are preferred electrolytes. The electrolyte is preferably present in a concentration of 0.1 M to 1.5 M, more preferably 0.1 M to 0.8 M. It is possible to perform an oxidation-reduction pair by adding iodine to the electrolyte of the invention, the concentration of iodine added being preferably 0.01 M to 0.2 M.

[0072] The solvent used in the gel electrolyte according to the invention is desirably a compound having a low viscosity and improving an ion mobility, or having a high dielectric constant and improving an effective carrier concentration so that good ionic conductivity is exerted. Such solvents are exemplified by carbonate compounds such as ethylene carbonate and propylene carbonate; heterocyclic compounds such as 3-methyl-2-oxazolidinone; ether compounds such as dioxane and diethyl ether; chain ethers such as ethylene glycol dialkyl ethers, propylene glycol dialkyl ethers, polyethylene glycol dialkyl ethers and polypropylene glycol dialkyl ethers; alcohols such as methanol, ethanol, ethylene glycol monoalkyl ethers, propylene glycol monoalkyl ethers, polyethylene glycol monoalkyl ethers, and polypropylene glycol monoalkyl ethers; polyhydric alcohols such as ethylene glycol, propylene glycol, polyethylene glycol, polypropylene glycol, and glycerin; nitrile compounds such as acetonitrile, glutaronitrile, methoxyacetonitrile, propionitrile, and benzonitrile; aprotic polar compounds such as dimethyl sulfoxide and sulfolane; and water. Of these, carbonate compounds such as ethylene carbonate and propylene carbonate; heterocyclic compounds such as 3-methyl-2-oxazolidinone; and nitrile compounds such as acetonitrile, glutaronitrile, methoxyacetonitrile, propionitrile, and benzonitrile are especially preferred.

[0073] The gel electrolyte according to the invention is preferably prepared by mixing monomers to form the crosslinked polymer, a polymerization initiator, an electrolyte and a solvent to form a solution, applying the solution onto a dye-carrying electrode as by casting, coating, dipping or impregnation, to thereby form a sol-like electrolyte layer on the electrode, and effecting radical polymerization for gelation to form a gel electrolyte layer.

[0074] When the gel electrolyte layer is formed by coating, a coating solution is first prepared by adding a coating modifier (e.g., a leveling agent) and other additives to the solution containing the monomers, polymerization initiator, and electrolyte in solvent. The coating solution is applied by suitable techniques, such as spin coating, dip coating, air knife coating, curtain coating, roller coating, wire bar coating, gravure coating, extrusion coating using the hopper described in USP 2,681,294, and multi-layer co-coating as described in USP 2,761,418, 3,508,947 and 2,761,791. Thereafter, radical polymerization is carried out to form a gel electrolyte. The polymerization temperature may be determined as appropriate depending on the half-life temperature of the initiator, the heat resistant temperature of the dye, and the like although an appropriate temperature is often 10 to 150°C. When a compound in reduced state such as iodine is introduced into the electrolyte, this compound can serve as a polymerization inhibitor to inhibit polymerization of the monomers. The compound in reduced state such as iodine may be introduced into the gel electrolyte after its formation by a technique of placing a sample containing the gel electrolyte and the compound in reduced state such as iodine in a sealed container, and allowing the compound to diffuse into the gel electrolyte. The compound in reduced state such as iodine can also be incorporated into the device by coating or vapor depositing the compound to the counter electrode.

[0075] The counter electrode serves as a positive electrode in a photo-electrochemical cell. The counter electrode is usually of the same definition as the conductive support described above. In the case of a strength-sustainable construction, the support is not always necessary. The provision of the support is advantageous from the sealing aspect.

[0076] In order that light reach the photosensitive layer, at least one of the conductive support and the counter electrode must be substantially transparent. The photo-electrochemical cell of the invention favors the construction that the conductive support is transparent and sunlight is incident on the support side. Better results are obtained in this embodiment when the counter electrode has light reflecting property.

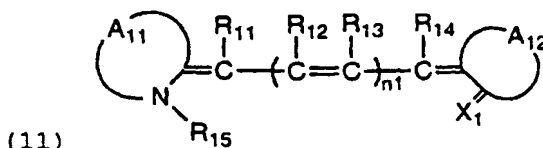
[0077] The counter electrode in the regenerative photo-electrochemical cell may be a glass or plastic member having a metal or conductive oxide evaporated thereon. Alternatively, a metal thin film may be formed by evaporation or sputtering to a thickness of up to 1  $\mu\text{m}$ , preferably 5 to 200 nm. In one preferred embodiment, a glass member having platinum evaporated thereon or a metal thin film formed by evaporation or sputtering is used as the counter electrode.

[0078] The photosensitive layer is designed in accordance with the intended application and may have a single layer construction or a multilayer construction. The dye in one photosensitive layer may be a single dye or a mixture of dyes.

[0079] In the regenerative photo-electrochemical cell of the invention, the side of the cell may be sealed with a polymer or adhesive for preventing oxidative degradation of the components.

## 10 Second Embodiment

[0080] In the second embodiment, the photoelectric conversion device of the invention is defined as comprising a photosensitive layer on a conductive support. The photosensitive layer contains semiconductor nanoparticulates sensitized with a polymethine dye or chromophore. The use of polymethine dyes ensures to fabricate dye-sensitized photoelectric conversion devices having improved conversion efficiency and is cost effective. The polymethine dyes used herein are represented by the general formulas (11), (12), (13) and (14).



[0081] In formula (11),  $R_{11}$ ,  $R_{12}$ ,  $R_{13}$ , and  $R_{14}$  each are hydrogen or monovalent substituents, with hydrogen being preferred. The monovalent substituents include alkyl (e.g., methyl, ethyl, isobutyl, n-dodecyl, cyclohexyl, vinyl, allyl, and benzyl), aryl (e.g., phenyl, tolyl, and naphthyl), heterocyclic residues (e.g., pyridyl, imidazolyl, furyl, thienyl, oxazolyl, thiazolyl, benzimidazolyl, and quinolyl), halogen atoms (e.g., fluoro, chloro and bromo), alkoxy (e.g., methoxy, ethoxy, and benzoyloxy), aryloxy (e.g., phenoxy), alkylthio (e.g., methylthio and ethylthio), arylthio (e.g., phenylthio), hydroxy and oxygen anions, nitro, cyano, amide (e.g., acetamino and benzoylamino), sulfonamide (e.g., methanesulfonylamino and benzenesulfonylamino), ureido (e.g., 3-phenylureido), urethane (e.g., isobutoxycarbonylamino and carbamoyloxy), ester (e.g., acetoxycarbonyl, benzoyloxy, methoxycarbonyl, and phenoxycarbonyl), carbamoyl (e.g., N-methylcarbamoyl and N,N-diphenylcarbamoyl), sulfamoyl (e.g., N-phenylsulfamoyl), acyl (e.g., acetyl and benzoyl), amino (e.g., amino, methylamino, anilino, and diphenylamino), sulfonyl (e.g., methylsulfonyl), phosphonyl and esters thereof, phosphonyloxy and esters thereof, carboxyl, and sulfo groups. These substituents may have such substituents attached to the carbon atom or atoms thereof.

[0082] The methine chain substituents represented by  $R_{11}$  to  $R_{14}$  may bond together to form a 3 to 9-membered monocyclic or polycyclic, aromatic, heterocyclic or alicyclic ring. Preferred rings are cyclobutene, cyclopentene, cyclohexene, benzene, dehydrodecalin, pyridine, dihydropyridine, tetrahydropyridine, furan, dihydrofuran, thiophene, dihydrothiophene, and hexahydroquinoline. All these rings may have fused thereto a 3 to 8-membered aromatic, heterocyclic or alicyclic ring. In formula (11),  $R_{15}$  is substituted or unsubstituted alkyl having 1 to 12 carbon atoms in total, examples of the alkyl and the substituent thereon being as defined for  $R_{11}$  to  $R_{14}$ .

[0083] In formula (11),  $A_{11}$  is a group of atoms to form a monocyclic or fused 3 to 9-membered ring with the carbon and nitrogen atoms. The atoms in the atom group to construct a ring are carbon, nitrogen, oxygen, sulfur, selenium and tellurium. The monocyclic or fused 3 to 9-membered ring that  $A_{11}$  forms with the carbon and nitrogen atoms may have substituents as mentioned above. Examples of the monocyclic or fused 3 to 9-membered ring that  $A_{11}$  forms with the carbon and nitrogen atoms include substituted or unsubstituted benzothiazoline, indoline, naphthothiazoline, and benzindoline.  $A_{12}$  is a group of atoms to form a monocyclic or fused 3 to 9-membered ring with the carbon atoms. The atoms in the atom group to construct a ring are carbon, nitrogen, oxygen, sulfur, selenium and tellurium. The monocyclic or fused 3 to 9-membered ring that  $A_{12}$  forms with the carbon atoms may have substituents as mentioned above. Substituted exo-methylene groups are also preferred substituents. The substituents on the substituted exo-methylene groups include cyano, carboxyl, sulfonyl and acyl groups. Examples of the substituted exo-methylene groups are dicyanomethylene, 1-cyano-1-carboxymethylene, 1-methanesulfonyl-1-carboxymethylene, and 1-cyano-1-acetylmethylene. The monocyclic or fused 3 to 9-membered ring that  $A_{12}$  forms with the carbon atoms is preferably substituted or unsubstituted rhodanine.

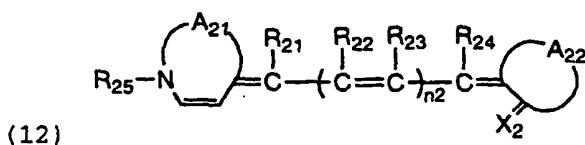
[0084]  $X_1$  is oxygen or sulfur.



[0085] In formula (11),  $n_1$  is an integer of 1 to 4. The length of methine chain is adjusted as appropriate for a particular purpose since it is correlated to the absorption wavelength of the dye such that the greater the value of  $n_1$ , the longer becomes the wavelength of light that the dye absorbs. From the standpoint of photoelectric conversion efficiency of sunlight, it is preferred that  $n_1$  be equal to 1.

[0086] The compound of formula (11) may have a counter ion depending on the overall electric charge of the molecule. The counter ion is not critical and may be either organic or inorganic. Typical examples include anions such as halide (e.g. fluoride, chloride, bromide and iodide ions), hydroxyl, perchlorate, tetrafluoroborate, hexafluorophosphate, acetate, trifluoroacetate, methanesulfonate, para-toluenesulfonate, and trifluoromethanesulfonate ions; and cations such as alkali metals (e.g., lithium, sodium and potassium), alkaline earth metals (e.g., magnesium and calcium), ammonium, alkyl ammonium (e.g., diethylammonium and tetrabutylammonium), pyridinium, alkyipyridinium (e.g., methylpyridinium), guanidinium, and tetraalkylphosphonium.

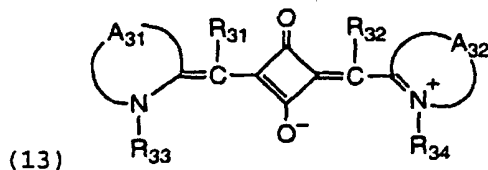
[0087] The compound of formula (11) has at least one carboxyl group as a substituent. It is especially preferred that the carboxyl group be attached directly or via an alkylene group to the heterocycle that  $A_{12}$  forms with the carbon atoms. The carboxyl group may form a salt with an alkali metal ion, ammonium or another organic cation. It may also form an intramolecular salt.



[0088] In formula (12),  $R_{21}$  to  $R_{24}$  are as defined for  $R_{11}$  in formula (11).  $R_{25}$  is as defined for  $R_{15}$  in formula (11).  $A_{21}$  is a group of atoms to form a monocyclic or fused 5 to 9-membered ring with the carbon and nitrogen atoms. The monocyclic or fused 5 to 9-membered ring that  $A_{21}$  forms with the carbon and nitrogen atoms is preferably dihydroquinoline.  $A_{22}$  is a group of atoms to form a monocyclic or fused 3 to 9-membered ring with the carbon atoms. The atoms in the atom group to construct a ring are carbon, nitrogen, oxygen, sulfur, selenium and tellurium. The monocyclic or fused 3 to 9-membered ring that  $A_{22}$  forms with the carbon atoms may have substituents as mentioned above. The substituents are the same as the substituents associated with  $A_{12}$  in formula (11). The monocyclic or fused 3 to 9-membered ring that  $A_{22}$  forms with the carbon atoms is preferably substituted or unsubstituted rhodanine.

[0089] In formula (12),  $n_2$  is an integer of 0 to 3. The length of methine chain is adjusted as appropriate for a particular purpose since it is correlated to the absorption wavelength of the dye such that the greater the value of  $n_2$ , the longer becomes the wavelength of light that the dye absorbs. From the standpoint of photoelectric conversion efficiency of sunlight, it is preferred that  $n_2$  be equal to 1.

[0090] The compound of formula (12) may have a counter ion as mentioned above, depending on the overall electric charge of the molecule. The compound of formula (12) has at least one carboxyl group as a substituent. It is especially preferred that the carboxyl group be attached directly or via an alkylene group to the heterocycle that  $A_{22}$  forms with the carbon atoms. The carboxyl group may form a salt with an alkali metal ion, ammonium or another organic cation. It may also form an intramolecular salt.

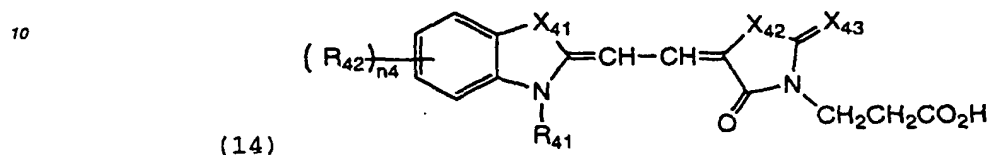


[0091] In formula (13),  $R_{31}$  and  $R_{32}$  are as defined for  $R_{11}$  in formula (11).  $R_{33}$  and  $R_{34}$  are as defined for  $R_{15}$  in formula (11).  $A_{31}$  is as defined for  $A_{11}$  in formula (11).  $A_{32}$  is a group of atoms to form a monocyclic or fused 3 to 9-membered ring with the carbon and quaternary nitrogen atoms. The atoms in the atom group to construct a ring are carbon, nitrogen, oxygen, sulfur, selenium and tellurium. The monocyclic or fused 3 to 9-membered ring that  $A_{32}$  forms with the carbon and nitrogen atoms may have substituents as mentioned above. Preferred examples of the monocyclic or fused

# EP 0 911 841 A2

3 to 9-membered ring that A<sub>32</sub> forms with the carbon and nitrogen atoms are quaternary salts of substituted or unsubstituted benzothiazoles, quaternary salts of substituted or unsubstituted indolenines, quaternary salts of substituted or unsubstituted naphthothiazoles and quaternary salts of substituted or unsubstituted benzindolenines.

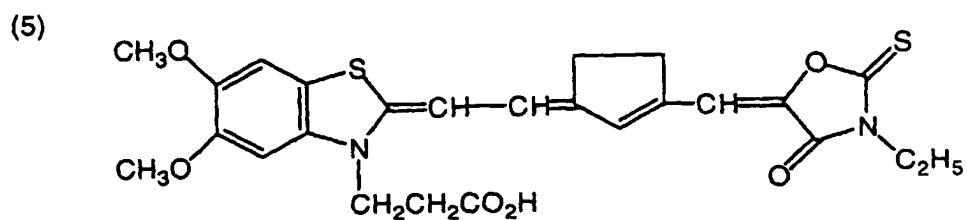
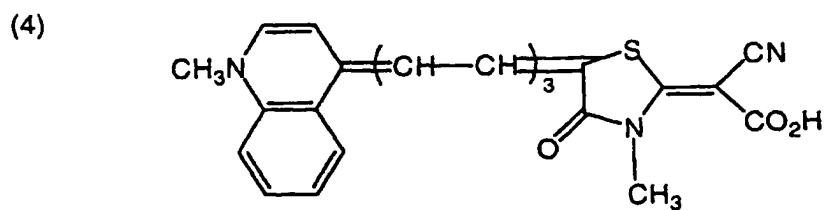
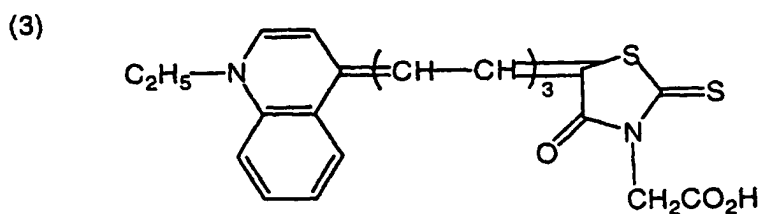
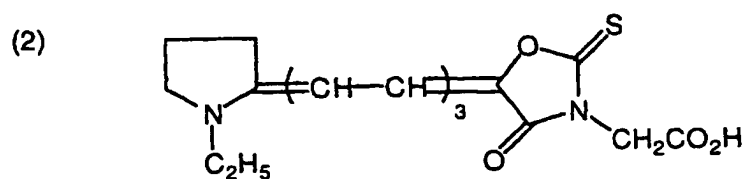
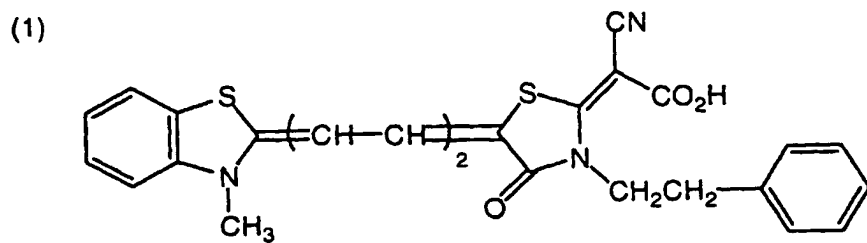
[0092] The compound of formula (13) may have a counter ion as mentioned above, depending on the overall electric charge of the molecule. The compound of formula (13) has at least one carboxyl group as a substituent. The carboxyl group may form a salt with an alkali metal ion, ammonium or another organic cation. It may also form an intramolecular salt.

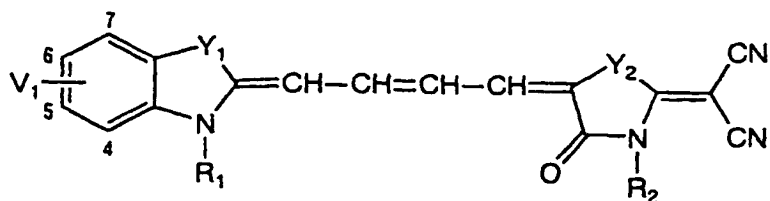



[0093] In formula (14), R<sub>41</sub> is as defined for R<sub>15</sub> in formula (11). R<sub>42</sub> is as defined for R<sub>11</sub> in formula (11). X<sub>41</sub> represents substituted or unsubstituted alkylene having 1 to 15 carbon atoms in total (e.g., methylene, ethylene, vinylene, and phenylene), substituted or unsubstituted alkylimino having 1 to 15 carbon atoms in total (e.g., methylimino, ethylimino, butylimino, and dodecylimino), arylimino (e.g., phenylimino), oxygen atoms, and sulfur atoms. Where these groups are substituted, such substituents are as defined for R<sub>11</sub> in formula (11). X<sub>41</sub> is preferably a sulfur atom. X<sub>42</sub> represents substituted or unsubstituted alkylimino groups having 1 to 15 carbon atoms in total, substituted or unsubstituted arylimino groups having 1 to 15 carbon atoms in total, oxygen atoms, and sulfur atoms. Where these groups are substituted, such substituents are as defined for R<sub>11</sub> in formula (11). X<sub>43</sub> is an oxygen or sulfur atom. It is preferred that both X<sub>42</sub> and X<sub>43</sub> be sulfur atoms. Letter n<sub>4</sub> is an integer of 0 to 4.

[0094] The compound of formula (14) may have a counter ion as mentioned above, depending on the overall electric charge of the molecule.

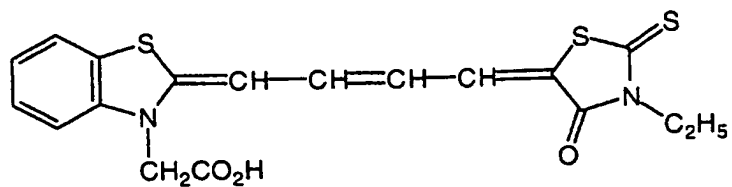
[0095] Preferred, non-limiting examples of the polymethine dyes of formulas (11) to (14) are given below.



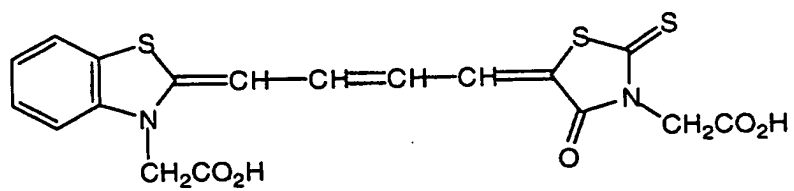


Compound	Y <sub>1</sub>	Y <sub>2</sub>	V <sub>1</sub>	R <sub>1</sub>	R <sub>2</sub>
(6)	S	S	H	C <sub>2</sub> H <sub>5</sub>	CH <sub>2</sub> CO <sub>2</sub> H
(7)	S	S	H	CH <sub>3</sub>	CH <sub>2</sub> CO <sub>2</sub> H
(8)	O	S	5-CH <sub>3</sub>	C <sub>2</sub> H <sub>5</sub>	(CH <sub>2</sub> ) <sub>2</sub> CO <sub>2</sub> H
(9)	O	O	6-CH <sub>3</sub>	CH <sub>3</sub>	 CO <sub>2</sub> H
(10)	NCH <sub>3</sub>	NCH <sub>3</sub>	5-CH <sub>3</sub> COO	C <sub>2</sub> H <sub>5</sub>	-CH <sub>2</sub> CO <sub>2</sub> H

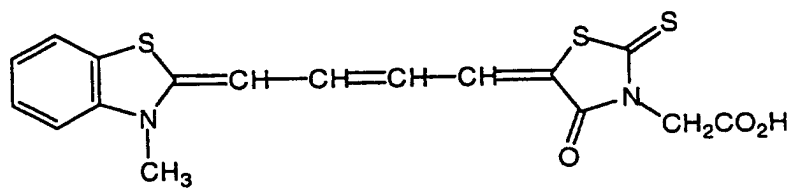
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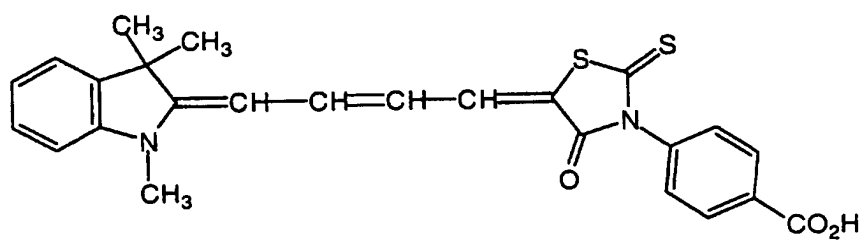
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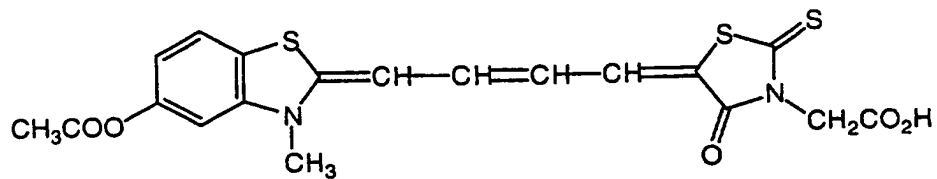
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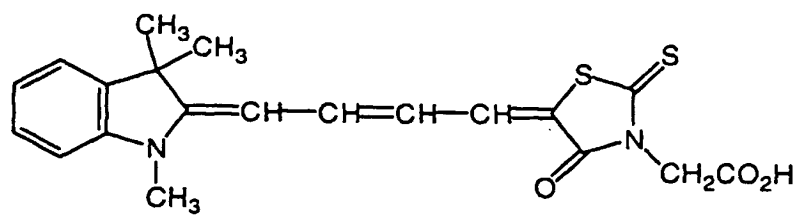
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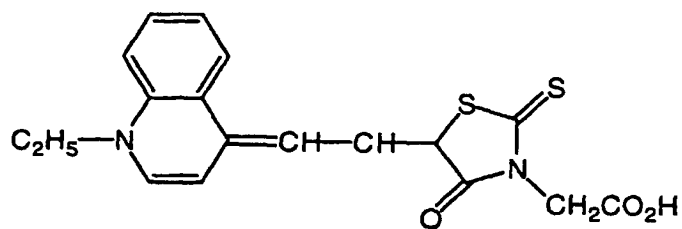
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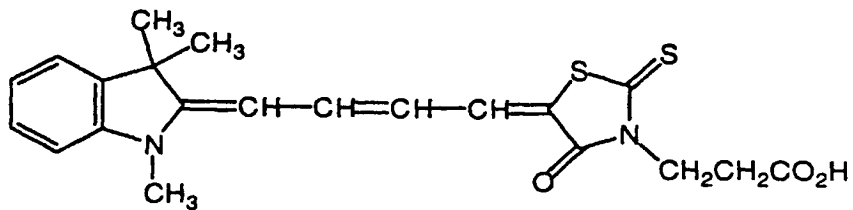
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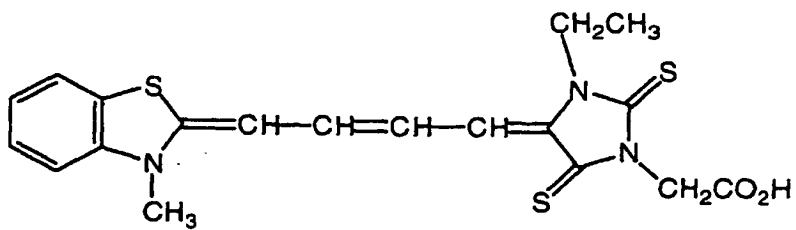
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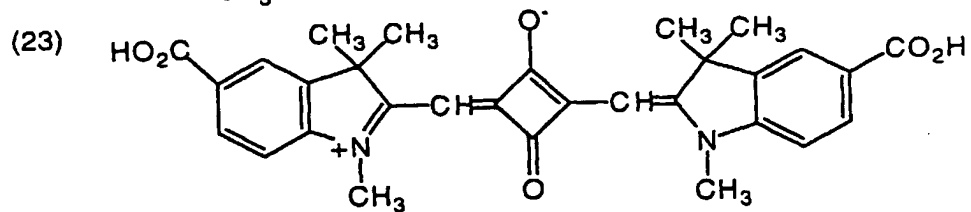
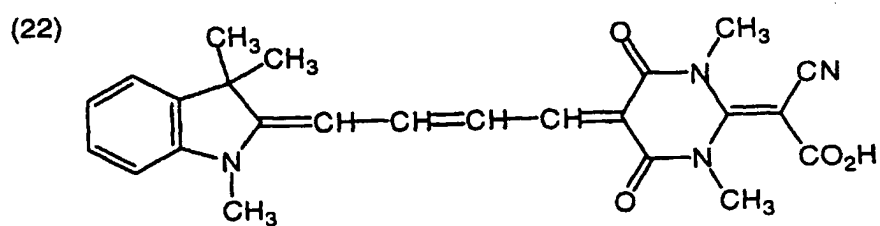
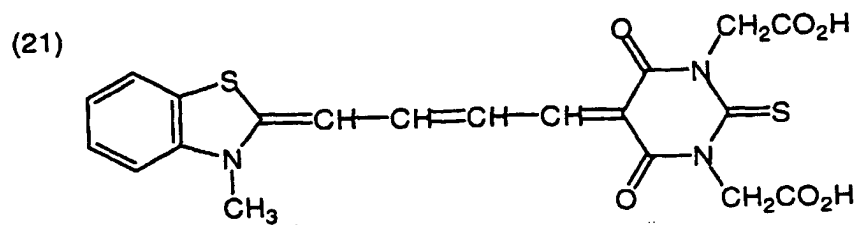
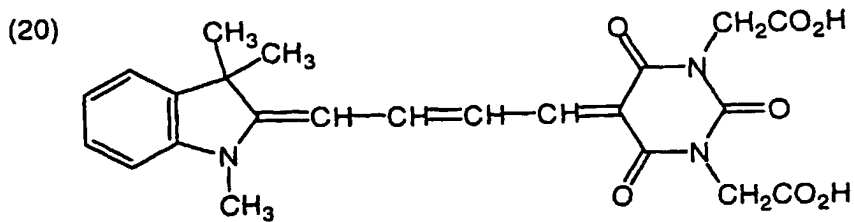


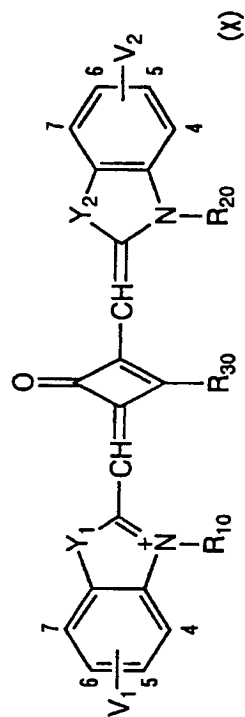
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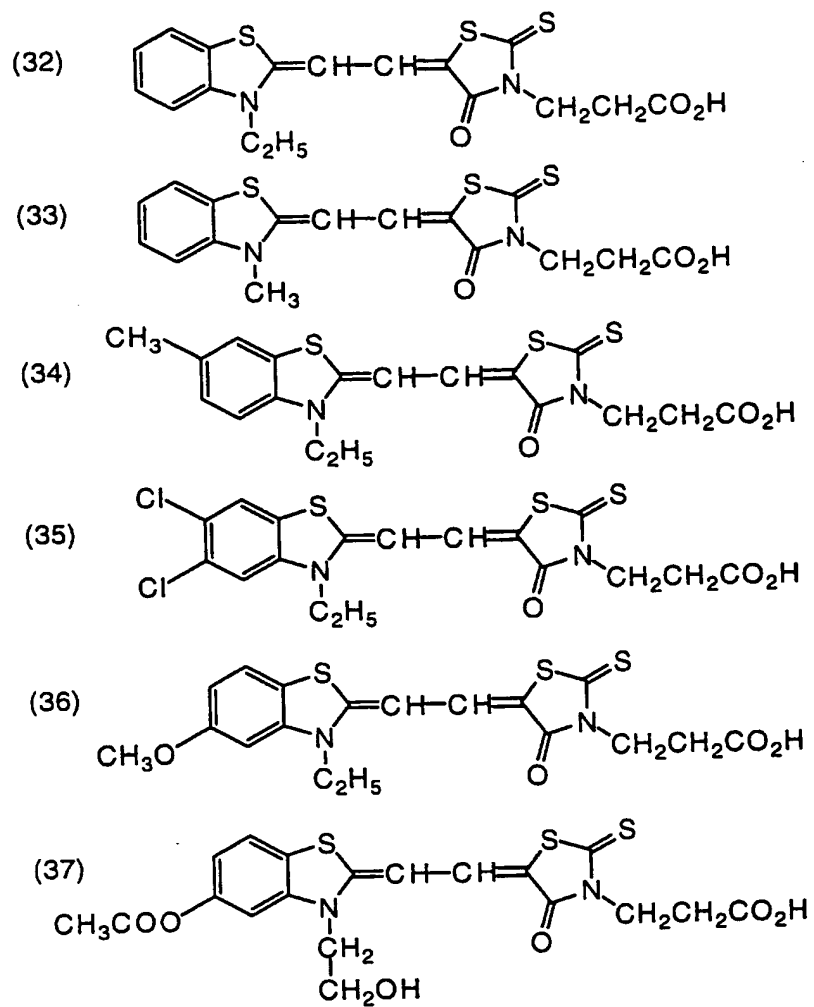


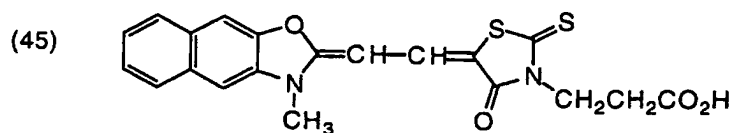
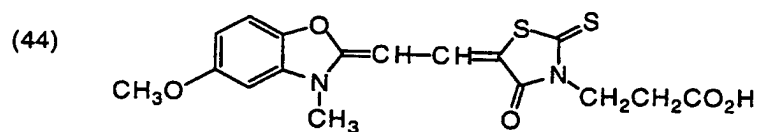
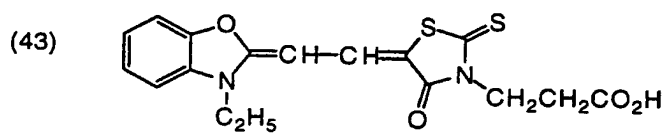
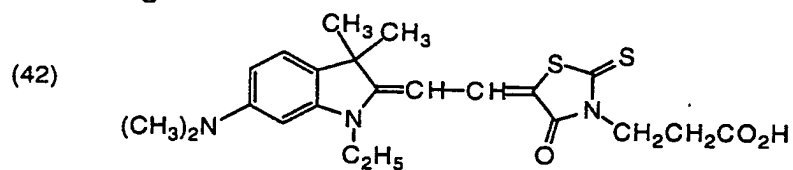
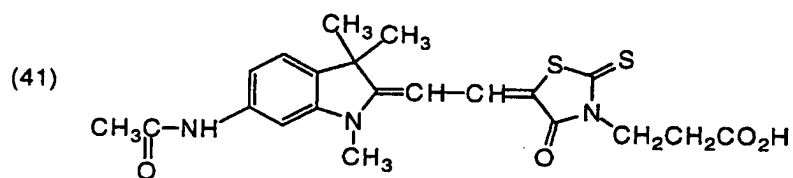
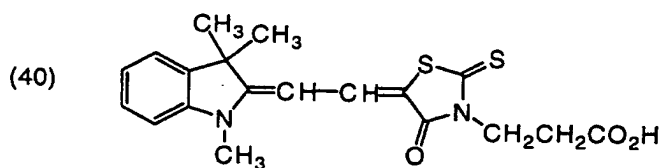
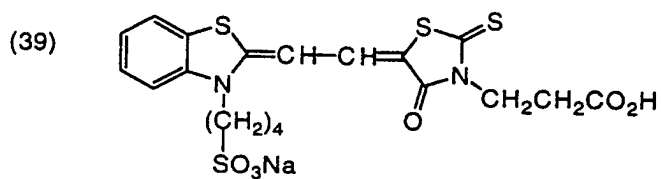
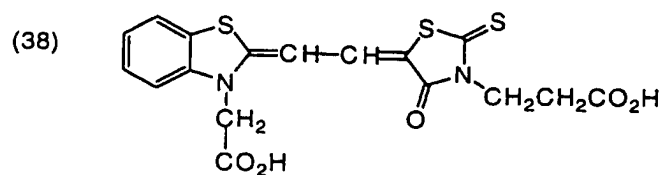


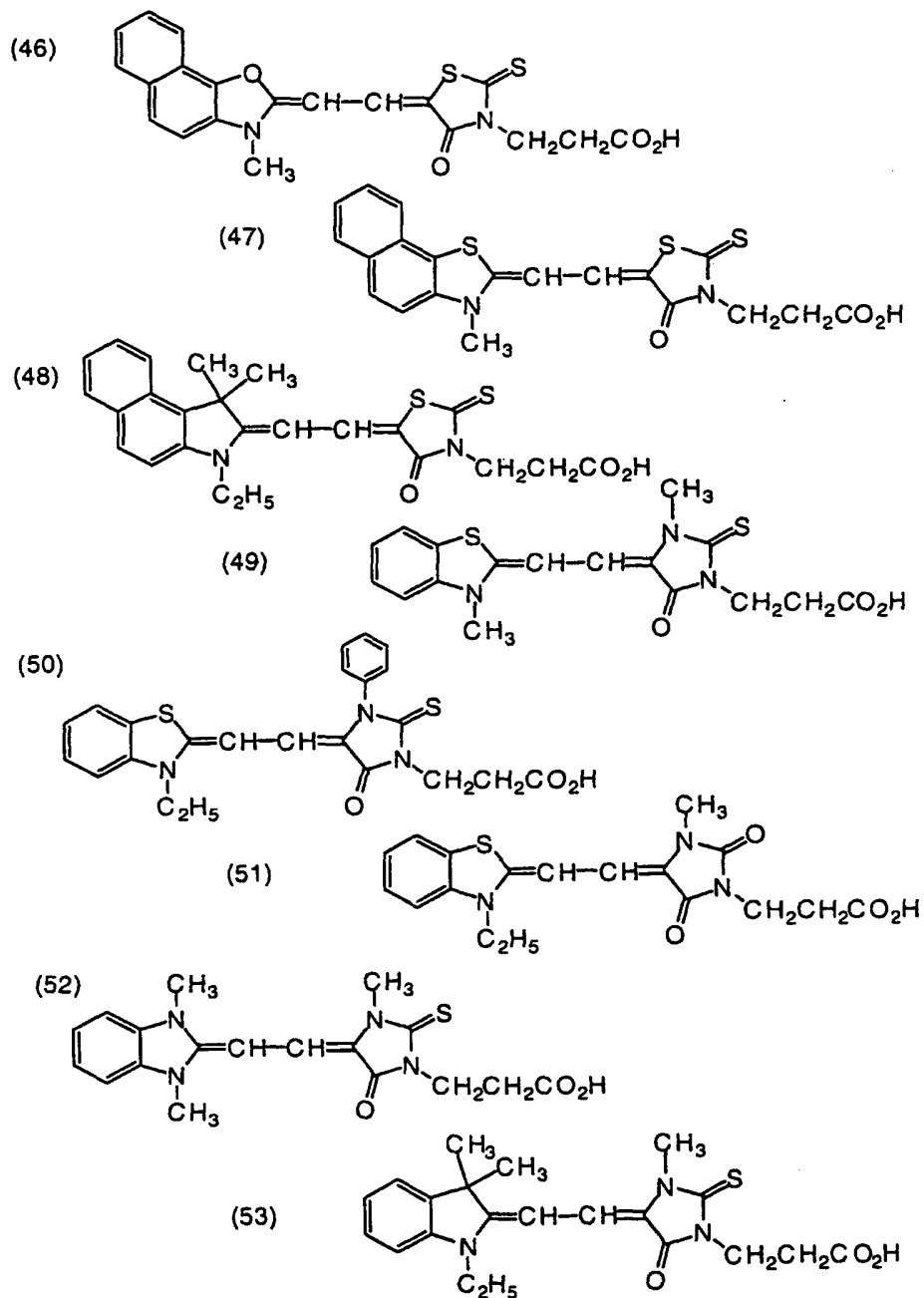


Compound	Y <sub>1</sub>	Y <sub>2</sub>	V <sub>1</sub>	V <sub>2</sub>	R <sub>10</sub>	R <sub>20</sub>	R <sub>30</sub>	X
(24)	S	S	5-COOH	5-COOH	C <sub>2</sub> H <sub>5</sub>	C <sub>2</sub> H <sub>5</sub>	O <sup>-</sup>	-
(25)	-CH=CH-	-CH=CH-	H	H	-(CH <sub>2</sub> ) <sub>2</sub> CO <sub>2</sub> H	-(CH <sub>2</sub> ) <sub>2</sub> CO <sub>2</sub> H	O <sup>-</sup>	-
(26)	-C(CH <sub>3</sub> ) <sub>2</sub> -	-C(CH <sub>3</sub> ) <sub>2</sub> -	5-COOH	5-COOH	C <sub>2</sub> H <sub>5</sub>	C <sub>2</sub> H <sub>5</sub>	O <sup>-</sup>	-
(27)	-C(CH <sub>3</sub> ) <sub>2</sub> -	-C(CH <sub>3</sub> ) <sub>2</sub> -	4,5-benzo	4,5-benzo	-(CH <sub>2</sub> ) <sub>2</sub> CO <sub>2</sub> H	-(CH <sub>2</sub> ) <sub>2</sub> CO <sub>2</sub> H	O <sup>-</sup>	-
(28)	S	S	6,7-benzo	6,7-benzo	-(CH <sub>2</sub> ) <sub>2</sub> CO <sub>2</sub> H	-(CH <sub>2</sub> ) <sub>3</sub> CO <sub>2</sub> H	O <sup>-</sup>	-
(29)	-C(CH <sub>3</sub> ) <sub>2</sub> -	-C(CH <sub>3</sub> ) <sub>2</sub> -	4,5-benzo	4,5-benzo	-(CH <sub>2</sub> ) <sub>2</sub> CO <sub>2</sub> H	-(CH <sub>2</sub> ) <sub>2</sub> CO <sub>2</sub> H	N(CH <sub>3</sub> ) <sub>2</sub>	I <sup>-</sup>
(30)	S	S	6,7-benzo	6,7-benzo	-(CH <sub>2</sub> ) <sub>3</sub> CO <sub>2</sub> H	-(CH <sub>2</sub> ) <sub>3</sub> CO <sub>2</sub> H	N(CH <sub>3</sub> ) <sub>2</sub>	I <sup>-</sup>
(31)	S	S	5-PO(OH) <sub>2</sub>	5-PO(OH) <sub>2</sub>	-CH <sub>2</sub> CO <sub>2</sub> H	-CH <sub>2</sub> CO <sub>2</sub> H	O <sup>-</sup>	-









[0096] The polymethine dyes of general formulae (11) and (12) can be synthesized by the methods described in F.M. Harmer, Heterocyclic Compounds - Cyanine Dyes and Related Compounds, John Wiley & Sons, New York, London,

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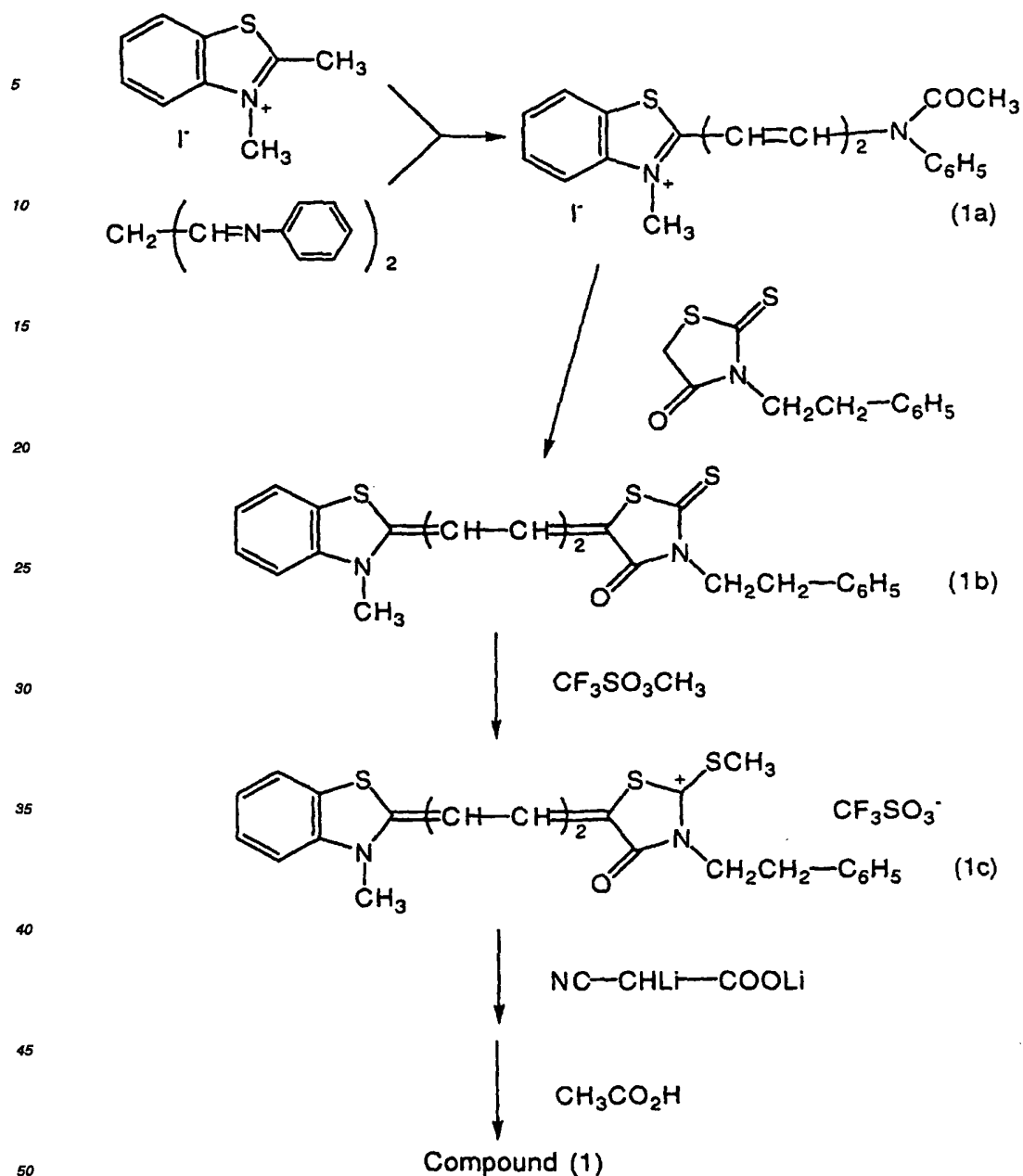
1964; D.M. Sturmer, Heterocyclic Compounds - Special topics in heterocyclic chemistry," Chap. 18, Sec. 14, pp. 482-515, John Wiley & Sons, New York, London, 1977; Rodd's Chemistry of Carbon Compounds, 2nd Ed., vol. IV, part B, 1977, Chap. 15, pp. 369-422, Elsevier Science Publishing Company Inc., New York; and British Patent No. 1,077,611.

**[0097]** The synthesis of the polymethine dyes used herein is illustrated by their synthesis examples. The synthesis examples are given for descriptive purpose only and not intended to limit the invention thereto.

Synthesis Example 1

Synthesis of Compound (1)

**[0098]** Compound (1) was synthesized by way of the synthesis route shown below.



**[0099]** To 150 ml of acetic anhydride were added 40 g of 2,3-dimethylbenzothiazolium iodide and 51 g of malondialdehyde bisphenylimine. The mixture was heated and stirred at 140°C for 2 hours. The reaction solution was poured into 1 liter of ethyl acetate whereupon crystals precipitated. Filtration yielded 45 g of a compound (1a).

**[0100]** In 100 ml of methanol were dissolved 20 g of compound (1a) and 9.1 g of N-(2-phenylethyl)rhodanine. To the solution was added 5.31 g of triethylamine. This was stirred at 50°C for 10 minutes whereupon crystals precipitated. Fil-

tration yielded 11.9 g of a compound (1b).

[0101] Compound (1b), 1.54 g, was dissolved in methylene chloride. To this solution at 10°C, 0.4 ml of methyl trifluoromethanesulfonate was gradually added dropwise to convert the compound (1b) to a compound (1c). In another container, 0.3 g of cyanoacetic acid was dissolved in 5 ml of tetrahydrofuran, and 3.6 ml of a solution containing 2 mol/liter of lithium diisopropylamide (by Aldrich Co.) was added at 10°C, yielding a light yellow suspension. The suspension was gradually added dropwise to the solution of compound (1c) at 0°C. The reaction solution was immediately poured into 200 ml of a 5% acetic acid aqueous solution whereupon 0.34 g of an end compound (1) was obtained in crystalline form.

[0102] Described below are the dye-sensitized photoelectric conversion device and photo-electrochemical cell of the invention to which the polymethine dyes are applied.

[0103] The dye-sensitized photoelectric conversion device of the invention is defined as comprising a conductive support and an electrode constructed by a layer (photosensitive layer) which is formed on the support by coating thereto semiconductor nanoparticulates having a polymethine dye adsorbed thereon. The photosensitive layer is designed in accordance with the intended application and may have a single layer construction or a multilayer construction. The dye in one photosensitive layer may be a single dye or a mixture of dyes. Light enters the photosensitive layer where it excites the dye. The excited dye possesses electrons of high energy, which are conveyed from the dye to the conduction band of the nanoparticulate semiconductor and then to the conductive support through diffusion. At this point, the dye molecules are in the oxidized state. The photo-electrochemical cell is designed such that electrons on the electrode perform work in an external circuit and then return to the dye in the oxidized state, while the dye-sensitized photoelectric conversion device serves as the negative electrode of the cell.

[0104] The conductive supports may be metal supports which themselves are electrically conductive or supports of glass or plastics having a conductive agent layer on their surface. In the latter case, the preferred conductive agents are metals such as platinum, gold, silver, copper, aluminum, rhodium, and indium, carbon, and conductive metal oxides such as indium-tin compound oxide and tin oxide doped with fluorine. The conductive agent layer is preferably about 0.05 to 10  $\mu\text{m}$  thick.

[0105] It is recommended that the conductive supports have a lower surface resistivity. The preferred range of surface resistivity is up to 50  $\Omega/\text{cm}^2$ , more preferably up to 10  $\Omega/\text{cm}^2$ . The lower limit is not critical although it is usually about 0.1  $\Omega/\text{cm}^2$ .

[0106] It is also recommended that the conductive supports be substantially transparent. The term "substantially transparent" means that the light transmittance of the support is at least 10%, preferably at least 50%, more preferably at least 80%. As the transparent conductive support, glass or plastic supports having conductive metal oxide coated thereon are preferable. The coverage or weight of conductive metal oxide coated is preferably 0.1 to 100 g per square meter of the glass or plastic support. Where transparent conductive supports are used, it is desired that light enters the device from the support side.

[0107] In the photosensitive layer, nanoparticulates of metal chalcogenides (e.g., oxides, sulfides and selenides) or perovskite may be used as the nanoparticulate semiconductor. Examples of the metal chalcogenides include oxides of titanium, tin, zinc, tungsten, zirconium, hafnium, strontium, indium, cerium, yttrium, lanthanum, vanadium, niobium, and tantalum, cadmium sulfide, and cadmium selenide. Examples of the perovskite are strontium titanate and calcium titanate. Of these, titanium oxide, zinc oxide, tin oxide and tungsten oxide are especially preferred.

[0108] The semiconductor nanoparticulates preferably have a mean particle size of 0.001 to 1  $\mu\text{m}$  expressed by the diameter of a circle of equivalent area to the projected area of a primary particle. When dispersed, the nanoparticulates have a mean particle size of 0.01 to 100  $\mu\text{m}$ .

[0109] Various methods are employable for coating semiconductor nanoparticulates to a conductive support. Exemplary methods are a method of applying a dispersion liquid or colloid solution of semiconductor nanoparticulates onto a conductive support, and a method of applying a semiconductor nanoparticulate precursor onto a conductive support and allowing the precursor to be hydrolyzed with moisture in air, thereby forming a semiconductor nanoparticulate coating. The dispersion liquid of semiconductor nanoparticulates can be prepared by such methods as grinding in a mortar, milling and dispersing in a mill, and synthesizing a semiconductor under such conditions that the semiconductor may precipitate in a solvent as nanoparticulates. The dispersing media may be water or various organic solvents such as methanol, ethanol, dichloromethane, acetone, acetonitrile, and ethyl acetate. In forming a dispersion, polymers, surfactants, acids or chelates may be used as the dispersant if necessary.

[0110] Semiconductor nanoparticulates are desired to have a greater surface area so that more dye may be adsorbed thereon. The semiconductor nanoparticulate layer as applied onto the support should preferably have a surface area which is greater than the projected area by a factor of at least 10, more preferably at least 100. No upper limit is imposed on the surface area although the upper limit is usually a multiplication factor of about 5,000.

[0111] In general, as the semiconductor nanoparticulate layer becomes thicker, the amount of the dye carried per unit projected area increases so that the capture rate of light becomes higher, but the loss by charge recombination becomes greater because the diffusion distance of generated electrons increases. For this reason, the semiconductor

nanoparticulate layer (i.e., photosensitive layer) has an appropriate range of thickness which is typically 0.1 to 100  $\mu\text{m}$ . When the semiconductor nanoparticulate layer is used in a photo-electrochemical cell, an appropriate thickness is 1 to 50  $\mu\text{m}$ , especially 3 to 30  $\mu\text{m}$ . After coating on a support, semiconductor nanoparticles may be fired at a temperature of about 100 to 800°C for about 10 minutes to about 10 hours in order to bring the particulates into close contact.

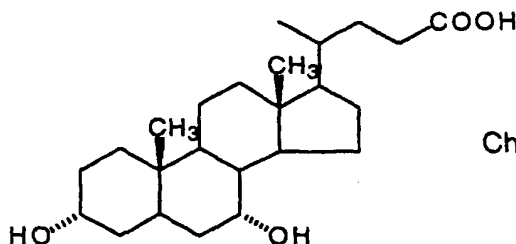
[0112] The coverage or weight of semiconductor nanoparticles coated is preferably 0.5 to 500 g, more preferably 5 to 100 g per square meter of the support.

[0113] In the second embodiment the semiconductor nanoparticles are sensitized by adsorption of the polymethine dye. Most often the dye is adsorbed to semiconductor nanoparticles by immersing fully dry semiconductor nanoparticles in a dye solution for a long period of time. The dye solution may be heated at 50 to 100°C if desired. The dye adsorption may be done either prior to or subsequent to the coating of semiconductor nanoparticles. It is also acceptable that semiconductor nanoparticles and the dye are simultaneously coated whereupon adsorption takes place. It is desirable to remove the unadsorbed dye by washing. Where the coated film is fired, it is preferred that the dye adsorption be done subsequent to firing. It is especially preferred that the dye is quickly adsorbed to the coated film after firing and before water adsorbs to the surface of the coated film. For adsorption, a single dye or a mixture of dyes may be used. In the latter case, there may be used a mixture of polymethine dyes according to the invention, or a mixture of a polymethine dye according to the invention and a complex dye as disclosed in USP 4,927,721, 4,684,537, 5,084,365, 5,350,644, 5,463,057, 5,525,440, and JP-A 249790/1995. For the application to photo-electrochemical cells, dyes are selected and mixed so as to make the wavelength range of photoelectric conversion as broad as possible.

[0114] The total amount of the dyes used is preferably 0.01 to 100 mmol, more preferably 0.1 to 50 mmol, and most preferably 0.5 to 10 mmol, per square meter of the support. The proportion of the polymethine dye used should preferably be at least 5 mol% of the entire dyes.

[0115] The amount of the dyes adsorbed to semiconductor nanoparticles is preferably 0.001 to 1 mmol, more preferably 0.1 to 0.5 mmol, per gram of the semiconductor nanoparticles. The amounts of the dye in these ranges ensure sufficient sensitization of the semiconductor. Less amounts of the dye would provide insufficient sensitization whereas excessive amounts of the dye would reduce the sensitization effect because of floating of the dye which is not adsorbed to the semiconductor.

[0116] Also for the purpose of reducing the association or interaction between dyes, a colorless compound may be co-adsorbed. Hydrophobic compounds to be co-adsorbed are steroid compounds having a carboxyl group, e.g., cholic acid, deoxycholic acid, and chenodeoxycholic acid shown below.



Chenodeoxycholic acid

[0117] After the adsorption of the dye, the semiconductor nanoparticles may be surface treated with amines. Preferred amines are pyridine, 4-tert-butylpyridine and polyvinylpyridine. The amines may be used as such if they are liquid or as solutions in organic solvents.

[0118] In the practice of the invention, the conductive agent and the nanoparticulate semiconductor may be in mixed state as a result of interdiffusion in proximity to the interface between the conductive support and the photosensitive layer.

[0119] The dye-sensitized photoelectric conversion device thus constructed can be applied to various sensors and photo-electrochemical cells. The application to photo-electrochemical cells requires an electric charge transfer layer and a counter electrode as shown in FIG. 2.

[0120] In FIG. 2, the photo-electrochemical cell 20 includes a photosensitive layer 23, an electric charge transfer layer 24 and a counter electrode 25 stacked on a conductive support 22 in the described order.

[0121] Now, the charge transfer layer and the counter electrode are described in detail.

[0122] The charge transfer layer has a function of supplementing electrons to the dye in the oxidized state. Typical examples include a solution of an oxidation-reduction pair in an organic solvent, a gel electrolyte wherein a polymer

matrix is impregnated with a solution of an oxidation-reduction pair in an organic solvent, and a molten salt containing an oxidation-reduction pair.

[0123] Examples of the oxidation-reduction pair include combinations of iodine with a iodide (e.g., lithium iodide, tetrabutyl ammonium iodide and tetrapropyl ammonium iodide), combinations of an alkylviologen (e.g., methylviologen chloride, hexylviologen bromide and benzylviologen tetrafluoroborate) with a reduced form thereof, combinations of a polyhydroxybenzene (e.g., hydroquinone and naphthohydroquinone) with an oxidized form thereof, and combinations of divalent and trivalent ion complexes (e.g., potassium ferricyanate and potassium ferrocyanate). Of these, the combinations of iodine with iodides are preferred. The organic solvents in which the oxidation-reduction pair is dissolved include aprotic polar solvents such as acetonitrile, propylene carbonate, ethylene carbonate, dimethylformamide, dimethyl sulfoxide, sulfolane, 1,3-dimethylimidazoline, and 3-methyloxazolidinone. The polymers used as the matrix of the gel electrolyte are, for example, polyacrylonitrile and polyvinylidene fluoride. Examples of the molten salt include lithium iodide and at least one lithium salt (such as lithium acetate or lithium perchlorate). The molten salt may be improved in fluidity at room temperature by mixing therewith a polymer such as polyethylene oxide. The amount of the polymer added to this end is usually 1 to 50% by weight.

[0124] The oxidation-reduction pair must be present in a sufficient concentration to become an electron carrier. When used in the solution or gel electrolyte form, the total concentration of the oxidation-reduction pair in the solution is preferably at least 0.01 mol/liter, more preferably at least 0.1 mol/liter, most preferably at least 0.3 mol/liter. The upper limit of concentration is not critical although it is usually about 5 mol/liter.

[0125] The counter electrode serves as a positive electrode in a photo-electrochemical cell. The counter electrode is usually of the same definition as the conductive support described above. In the case of a strength-sustainable construction, the support is not always necessary. The provision of the support is advantageous from the sealing aspect.

[0126] In order that light reach the photosensitive layer, at least one of the conductive support and the counter electrode must be substantially transparent. The photo-electrochemical cell of the invention favors the construction that the conductive support is transparent and sunlight is incident on the support side. Better results are obtained in this embodiment when the counter electrode has light reflecting property. The counter electrode in the photo-electrochemical cell may be a glass or plastic member having a metal or conductive oxide evaporated thereon. A glass member having platinum deposited thereon is especially preferred.

[0127] In the photo-electrochemical cell of the invention, the side of the cell may be sealed with a polymer or adhesive for preventing the components from evaporating off.

[0128] The thus obtained photo-electrochemical cell, as measured at AM 1.5G and 100 mW/cm<sup>2</sup>, exhibits an open voltage of 0.01 to 3 volts, a short-circuit current density of 0.001 to 20 mA/cm<sup>2</sup>, a form factor of 0.1 to 0.99, and a conversion efficiency of 0.001 to 25%.

#### EXAMPLE

[0129] Examples of the invention are given below for illustrating the preparation of a dye-sensitized photoelectric conversion device and a regenerative photo-electrochemical cell according to the invention, but the invention is not limited to these examples.

#### Example 1

##### 1. Preparation of titanium dioxide dispersion

[0130] A stainless steel vessel having an internal volume of 200 ml and lined on the inside surface with Teflon was charged with 15 g of titanium dioxide (Degussa P-25 by Nippon Aerosil K.K.), 45 g of water, 1 g of a dispersant (Triton X-100 by Aldrich), and 30 g of zirconia beads having a diameter of 0.5 mm (Nikkato K.K.). Using a sand grinder mill (Imex K.K.), the contents were dispersed at 1,500 rpm for 2 hours. The zirconia beads were removed from the dispersion by filtration.

##### 2. Preparation of dye-adsorbed TiO<sub>2</sub> electrode (Electrode A)

[0131] On the conductive surface side of a conductive glass piece coated with fluorine-doped tin oxide (TCO glass by Asahi Glass K.K. cut to 20 mm x 20 mm), the dispersion prepared above was applied using a glass bar. More particularly, eight glass pieces were closely arranged in two columns (2x4) with the conductive surface side faced upward. Adhesive tape strips were attached to opposite end portions (3 mm from the end) of the two columns of glass pieces. The dispersion was applied to the set of eight glass pieces between the tape strips and spread thereon by sliding a glass bar on the parallel tape strips which serve as a spacer and mask. After application, the adhesive tape strips were peeled off, and the coating was air dried for one day at room temperature. The end portions where the adhesive tape



strips had been attached were later used to provide electrical connection with a tester for the measurement of photo-current. Next, the glass pieces were placed in an electric furnace (muffle furnace Model FP-32 by Yamato Science K.K.) where they were fired at 450°C for 30 minutes. The glass pieces were taken out and cooled down whereupon they were immersed for 3 hours in an ethanol solution containing  $3 \times 10^{-4}$  mol/l of a dye as shown in Table 2. The dye-adsorbed glass pieces were immersed in 4-tert-butylpyridine for 15 minutes, washed with ethanol and air dried.

### 3. Synthesis of gel electrolyte and fabrication of photo-electrochemical cell

#### 3-1. Synthesis of monomer (1): ethylene glycol ethyl carbonate methacrylate

[0132] A 500-ml three-necked glass flask equipped with a stirrer, thermometer, and reflux condenser was charged with 26.0 g (0.2 mol) of hydroxyethyl methacrylate, 17.4 g (0.22 mol) of pyridine, and 150 ml of tetrahydrofuran. With an ice bath, the flask was cooled to a temperature of 0 to 5°C, and 23.9 g (0.22 mol) of ethyl chloroformate was added dropwise to the reaction system over 30 minutes. The reaction system was then heated at 60°C and stirred for 2 hours.

[0133] After the reaction solution was cooled to room temperature, it was subjected to separation and extraction using ethyl acetate and ion-exchanged water, and magnesium sulfate was added to the ethyl acetate layer. The ethyl acetate layer was concentrated and then distilled in vacuum, yielding 40.4 g (yield about 59%) of the above monomer.

[0134] Carbonate group-containing monomers having similar structures were similarly synthesized.

#### 3-2. Synthesis of monomer (2): N-vinyl-N'-ethylimidazolium iodide

[0135] A 200-ml three-necked glass flask equipped with a stirrer, thermometer, and reflux condenser was charged with 50 g (0.32 mol) of ethane iodide and 0.1 g of nitrobenzene. With stirring at room temperature, 7.5 g (0.08 mol) of vinyl imidazole was added dropwise to the reaction system over 20 minutes. The reaction system was then heated at 80°C and stirred for 4 hours.

[0136] After the reaction solution was cooled to room temperature, it was worked up by silica gel chromatography (mobile phase: methylene chloride/methanol = 8/2), obtaining 15.8 g (yield about 79%) of the above compound as yellow crystals.

[0137] Quaternary ammonium salt-containing monomers having similar structures were similarly synthesized.

#### 3-3. Fabrication of photo-electrochemical cell comprising a gel electrolyte layer

[0138] By mixing 60 mg of ethylene glycol ethyl carbonate methacrylate, 60 mg of 2-ethoxyethyl methacrylate, 20 mg of tri(ethylene glycol) dimethacrylate, 1.43 mg (1 wt% based on the monomers) of dimethyl-2,2'-azobis(2-methyl propionate) as a polymerization initiator, 1.86 g of 3-methyl-2-oxazolidinone, and 0.112 g of lithium iodide, a homogeneous solution was obtained. Argon gas was bubbled into the solution for 5 minutes. After a counter electrode having platinum deposited thereon was rested on a dye-carrying TiO<sub>2</sub> electrode, the solution was introduced into this assembly under the impetus of an osmotic pressure. The assembly was heated at 85°C for 3 hours in an argon atmosphere for converting the electrolyte into a gel, obtaining a photo-electrochemical cell.

[0139] Cells were also fabricated by repeating the above steps while changing the combination of the dye and the gel electrolyte as shown in Table 2.

[0140] The cells fabricated in this example are photo-electrochemical cells in which a conductive glass 1 (having a conductive layer 2), a TiO<sub>2</sub> electrode 3, a dye layer 4, a gel electrolyte layer 5, a counter electrode 6, and a platinum-deposited glass plate 7 are stacked in the described order as shown in FIG. 1.

Table 2

No.	Dye	Gel electrolyte		Supporting electrolyte		Solvent	
		Type	Concentration (wt%)	Type	Concentration (mol/l)	Type	Amount (wt%)
1	R-1	P-1	15%	LiI	0.3	NMO	85%
2	S-11	P-3	15%	LiI	0.6	PC/NMO=1/1	85%
3	R-1	P-4	15%	LiI	0.3	NMO/DME=1/1	85%
4	S-11	P-6	5%	LiI	0.4	NMO/EC=1/1	95%
5	R-1	P-6	15%	LiI	0.6	NMO	85%
6	R-1	P-6	30%	(C <sub>3</sub> H <sub>7</sub> ) <sub>4</sub> NI	0.5	NMO	70%
7	R-2	P-6	20%	LiI	0.5	NMO	80%
8	S-11	P-6	10%	(C <sub>3</sub> H <sub>7</sub> ) <sub>4</sub> NI	0.5	NMO	90%
9	S-22	P-6	50%	LiI	0.5	NMO	50%
10	R-1	P-6	15%	LiI	0.5	NMO	85%
11	R-1	P-7	20%	LiI	0.5	NMO	80%
12	R-1	P-9	15%	LiI	0.7	NMO	85%
13	S-11	P-10	15%	LiI	0.5	NMO	85%
14	R-6	P-11	15%	(C <sub>3</sub> H <sub>7</sub> ) <sub>4</sub> NI	0.5	NMO/EC=1/1	85%
15	R-9	P-11	2%	LiI	0.5	NMO	98%
16	S-1	P-13	30%	LiI	0.5	NMO	70%
17	S-11	P-17	10%	LiI	0.5	NMO	90%
18	S-12	P-18	10%	LiI	0.5	NMO	90%
19	S-16	P-19	15%	LiI	0.8	NMO	85%
20	S-18	P-20	15%	LiI	0.5	NMO	85%
21	S-19	P-21	15%	(C <sub>3</sub> H <sub>7</sub> ) <sub>4</sub> NI	0.5	NMO	85%
22	S-12	P-23	15%	(C <sub>3</sub> H <sub>7</sub> ) <sub>4</sub> NI	0.5	NMO	85%
23	S-26	P-24	80%	LiI	0.5	NMO	20%
24	R-1	P-25	15%	LiI	0.5	PC/DME=1/1	85%
25	S-11	P-26	5%	LiI	0.7	NMO	95%
26	R-1	P-27	15%	(C <sub>3</sub> H <sub>7</sub> ) <sub>4</sub> NI	0.5	NMO	85%
27	R-1	P-29	15%	LiI	0.5	NMO	85%
28	R-1	P-30	15%	LiI	0.5	NMO	85%

Note: NMO: 3-methyl-2-oxazolidinone PC: propylene carbonate  
 EC: ethylene carbonate DME: dimethoxyethane

Measurement of photoelectric conversion efficiency

[0141] Light of a 500-W xenon lamp (Ushio K.K.) was passed through a AM 1.5 filter (by Oriel Co.) and a sharp cut filter Kenko L-42, obtaining simulated sunlight free of ultraviolet radiation. The intensity of light was 86 mW/cm<sup>2</sup>.

[0142] With clips connected to the conductive glass substrate of the photoelectric conversion device and the platinum-deposited glass member, the simulated sunlight was irradiated to the cell. The electricity generated in the cell was measured by a current-voltage tester (Keithley SMU238). The open circuit voltage (Voc), short-circuit current density (Jsc), fill factor (ff), and conversion efficiency ( $\eta$ ) of this solar battery were reported in Table 3 along with the short-circuit current density after 120 hours of continuous irradiation and a percent drop thereof. Note that the percent drop of short-circuit current density is calculated according to  $[1 - (Jsc \text{ after } 120 \text{ hr.}) / (\text{initial } Jsc)] \times 100$ . Additionally, the film surface was examined for tack. The results are shown in Table 3.

Comparative Example 1

[0143] On the dye-sensitized TiO<sub>2</sub> electrode substrate (Electrode A, 20 mm x 20 mm) prepared in Example 1 was rested a platinum-deposited glass member of the same size (see FIG. 1). By utilizing a capillary phenomenon, an electrolytic solution was penetrated into the interface or space between the glass plates. The electrolytic solution contained 0.05 mol/l of iodine and 0.5 mol/l of lithium iodide in a mixture of acetonitrile and 3-methyl-2-oxazolidinone in a volume ratio of 90:10. A comparative photo-electrochemical battery A was fabricated in this way.

Comparative Example 2

[0144] A mix solution was prepared by mixing 1 g of hexaethylene glycol methacrylate (Blenmer PE350 by Nippon Oil & Fats K.K.), 1 g of ethylene glycol, and 20 mg of 2-hydroxy-2-methyl-1-phenyl-propan-1-one (Darocure 1173 by Nippon Ciba Geigy K.K.) as a polymerization initiator, dissolving 500 mg of lithium iodide in the solution, and deaerating in vacuum for 10 minutes. This mix solution was applied onto the dye-sensitized TiO<sub>2</sub> electrode substrate (Electrode A, 20 mm x 20 mm) prepared in Example 1. The porous material having the mix solution coated thereon was placed in vacuum for removing bubbles from the porous material and helping the monomer to penetrate. Thereafter, ultraviolet radiation was irradiated to effect polymerization, thereby distributing a uniform gel of polymer in pores of the porous material. The thus obtained material was exposed to an iodine atmosphere for 30 minutes whereby iodine was diffused into the polymer. A comparative photo-electrochemical battery B was fabricated in this way.

Comparative Example 3

[0145] A mix solution was prepared by mixing 1 g of hexaethylene glycol methacrylate (Blenmer PE350 by Nippon Oil & Fats K.K.), 100 mg of tetraethylene glycol diacrylate, 3 g of propylene carbonate as a solvent in which the electrolyte could be dissolved, and 20 mg of 2-hydroxy-2-methyl-1-phenyl-propan-1-one (Darocure 1173 by Nippon Ciba Geigy K.K.) as a polymerization initiator, dissolving 500 mg of lithium iodide in the solution, and deaerating in vacuum for 10 minutes. This mix solution was applied onto the dye-sensitized TiO<sub>2</sub> electrode substrate (Electrode A, 20 mm x 20 mm) prepared in Example 1. The porous material having the mix solution coated thereon was placed in vacuum for removing bubbles from the porous material and helping the monomer to penetrate. Thereafter, ultraviolet radiation was irradiated to effect polymerization. The thus obtained device was exposed to an iodine atmosphere for 30 minutes. A comparative photo-electrochemical battery C was fabricated in this way.

[0146] These comparative batteries A, B, and C were tested as in Example 1. The results are also shown in Table 3.

Table 3

No.	Jsc ( $\mu\text{A}/\text{cm}^2$ )	Voc (V)	ff	$\eta$ (%)	Jsc after 120 hr.	Jsc drop (%)	Surface tack
1	216	0.60	0.67	0.10	184	15	tack-free
2	416	0.65	0.70	0.22	362	13	tack-free
3	230	0.70	0.64	0.12	189	18	tack-free
4	216	0.62	0.72	0.11	199	8	tack-free
5	523	0.75	0.66	0.30	492	6	tack-free
6	236	0.72	0.65	0.13	229	3	tack-free

EP 0 911 841 A2

Table 3 (continued)

No.	Jsc ( $\mu\text{A}/\text{cm}^2$ )	Voc (V)	ff	$\eta$ (%)	Jsc after 120 hr.	Jsc drop (%)	Surface tack
7	387	0.68	0.69	0.21	325	16	tack-free
8	264	0.64	0.63	0.12	224	15	tack-free
9	326	0.68	0.60	0.15	271	17	tack-free
10	486	0.62	0.59	0.21	408	16	tack-free
11	373	0.58	0.71	0.18	328	12	tack-free
12	449	0.66	0.70	0.24	368	18	tack-free
13	342	0.53	0.68	0.14	287	16	tack-free
14	232	0.70	0.63	0.12	197	15	tack-free
15	413	0.69	0.66	0.22	355	14	tack-free
16	262	0.63	0.67	0.13	215	18	tack-free
17	335	0.72	0.60	0.17	281	16	tack-free
18	254	0.63	0.58	0.11	211	17	tack-free
19	249	0.68	0.70	0.14	212	15	tack-free
20	320	0.69	0.63	0.16	291	9	tack-free
21	286	0.72	0.62	0.15	255	11	tack-free
22	233	0.62	0.63	0.11	179	23	tack-free
23	287	0.63	0.64	0.13	232	19	tack-free
24	319	0.70	0.66	0.17	268	16	tack-free
25	253	0.60	0.62	0.11	220	13	tack-free
26	212	0.68	0.69	0.12	187	12	tack-free
27	352	0.70	0.69	0.20	313	11	tack-free
28	316	0.68	0.61	0.15	259	18	tack-free
Comparative solar battery A	2800	0.60	0.43	0.84	252	91	tacky (liquid)
Comparative solar battery B	153	0.35	0.50	0.03	101	34	tacky
Comparative solar battery C	198	0.42	0.58	0.06	152	23	tacky

[0147] As compared with wet solar batteries of Comparative Examples, the batteries in Example 1 experience little deterioration of photoelectric conversion properties and little change with time and remain tack-free on their surface.

Example 2

Preparation of titanium dioxide dispersion

[0148] A stainless steel vessel having an internal volume of 200 ml and lined on the inside surface with Teflon was charged with 15 g of titanium dioxide (Degussa P-25 by Nippon Aerosil K.K.), 45 g of water, 1 g of a dispersant (Triton X-100 by Aldrich), and 30 g of zirconia beads having a diameter of 0.5 mm (Nikkato K.K.). Using a sand grinder mill (Imex K.K.), the contents were dispersed at 1,500 rpm for 2 hours. The zirconia beads were removed from the dispersion by filtration. The dispersed titanium dioxide had a mean particle size of 2.5  $\mu\text{m}$  as measured by Master Sizer by Malvern.

Fabrication of photoelectric conversion device

[0149] On the conductive surface side of a conductive glass piece coated with fluorine-doped tin oxide (TCO glass by Asahi Glass K.K. cut to 20 mm x 20 mm), the dispersion prepared above was applied using a glass bar. The conductive glass had a surface resistivity of about  $30 \Omega/\text{cm}^2$ . More particularly, eight glass pieces were closely arranged in two columns (2x4) with the conductive surface side faced upward. Adhesive tape strips were attached to opposite end portions (3 mm from the end) of the two columns of glass pieces. The dispersion was applied to the set of eight glass pieces between the tape strips and spread thereon by sliding a glass bar on the parallel tape strips which serve as a spacer and mask. After application, the coating was air dried for one day at room temperature and the adhesive tape strips were peeled off. The end portions where the adhesive tape strips had been attached were later used to provide electrical connection with a tester for the measurement of photocurrent. Next, the glass pieces were placed in an electric furnace (muffle furnace Model FP-32 by Yamato Science K.K.) where they were fired at  $450^\circ\text{C}$  for 30 minutes. The glass pieces were taken out and cooled down whereupon they were immersed for 3 hours in an ethanol solution containing  $3 \times 10^{-4} \text{ mol/l}$  of an inventive dye as shown in Table 4. The dye-adsorbed glass pieces were immersed in a 10 wt% ethanol solution of 4-tert-butylpyridine for 30 minutes, washed with ethanol and air dried. The thus obtained photosensitive layer was  $10 \mu\text{m}$  thick, and the weight of semiconductor nanoparticulates coated was  $20 \text{ g/m}^2$ . Depending on the type of dye, the weight of the dye coated was selected as appropriate in the range of 0.1 to  $10 \text{ mmol/m}^2$ .

Measurement of reflection spectrum

[0150] The photoelectric conversion device was measured for reflection spectrum using a spectrophotometer equipped with an integrating sphere (U-3500 by Hitachi K.K.). Table 4 shows the wavelength and absorbance of an absorption peak situated on the longest wavelength side.

Fabrication of photo-electrochemical cell

[0151] There was fabricated a photo-electrochemical cell of the structure shown in FIG. 3 which is a modification of the structure shown in FIG. 2. The cell 30 of FIG. 3 utilizes the photoelectric conversion device comprising a photosensitive layer 33 on a conductive support which has a conductive agent layer 32 on a glass support 31. An electrolytic solution layer 34 serving as a charge transfer layer is situated on the photosensitive layer 33. A platinum-deposited glass plate 35 is rested thereon as a counter electrode. In the fabrication process, the platinum-deposited glass plate of the same size was rested on the photoelectric conversion device (see FIG. 3). Actually, they were offset such that the uncoated portion of the photoelectric conversion device might not contact the platinum-deposited glass plate. By utilizing a capillary phenomenon, an electrolytic solution was penetrated into the interface or space between the glass plates. The electrolytic solution contained 0.05 mol/l of iodine and 0.5 mol/l of lithium iodide in a mixture of acetonitrile and N-methyl-2-oxazolidinone in a volume ratio of 90:10.

Measurement of photoelectric conversion efficiency

[0152] Light of a 500-W xenon lamp (Ushio K.K.) was passed through a AM 1.5G filter (by Oriel Co.) and a sharp cut filter Kenko L-42, obtaining simulated sunlight free of ultraviolet radiation. The intensity of light was  $50 \text{ mW/cm}^2$ .

[0153] While the simulated sunlight was irradiated to the photoelectric conversion device, the electricity generated in the cell was measured by a current-voltage tester (Keithley SMU238). The open circuit voltage (Voc), short-circuit current density (Jsc), fill factor (ff), and conversion efficiency ( $\eta$ ) of this photochemical cell were reported in Table 4.

Table 4

Sample No.	Polymethine dye	Maximum of absorption (nm)	Absorbance	Voc (V)	Jsc ( $\text{mA/cm}^2$ )	ff	$\eta$ (%)
201	(1)	648	0.75	0.48	0.43	0.58	0.23
202	(15)	663	1.10	0.37	0.50	0.45	0.17
203	(16)	613	0.70	0.35	0.31	0.48	0.10
204	(17)	614	0.80	0.58	0.50	0.51	0.29
205	(23)	636	0.89	0.38	0.39	0.42	0.12
206	(32)	649	1.20	0.56	5.1	0.51	2.91

**Example 3**

[0154] Photoelectric conversion devices (sample Nos. 207 to 212) were fabricated as in Example 2 except that  $3 \times 10^{-3}$  mol/l of chenodeoxycholic acid was added to the dye solution whereby the dye and chenodeoxycholic acid were co-adsorbed on surfaces of semiconductor nanoparticulates. They were tested as in Example 2, with the results shown in Table 5.

Table 5

Sample No.	Polymethine dye	Voc (V)	Jsc (mA/cm <sup>2</sup> )	ff	$\eta$ (%)
207	(1)	0.51	1.20	0.61	0.77
208	(15)	0.43	1.09	0.53	0.50
209	(16)	0.42	0.88	0.54	0.40
210	(17)	0.61	1.51	0.58	1.06
211	(23)	0.58	4.3	0.62	3.09
212	(32)	0.56	5.1	0.52	2.97

[0155] As seen from Table 4, all the inventive dyes show excellent photoelectric conversion properties. As seen from Table 5, the addition of chenodeoxycholic acid to the dye solution is effective for improving photoelectric conversion properties. An outstanding improvement was made with compound (23) falling in the scope of formula (13).

[0156] The first embodiment of the invention provides a photoelectric conversion device which has improved photoelectric conversion properties, is minimized in leakage of electrolytic solution and deterioration with time of properties concomitant therewith, and is tack-free on its surface.

[0157] According to the second embodiment of the invention, a photoelectric conversion device comprising a specific organic dye for sensitization is provided. Using the photoelectric conversion device, a photo-electrochemical cell can be constructed.

[0158] Reasonable modifications and variations are possible from the foregoing disclosure without departing from either the spirit or scope of the present invention as defined by the claims.

**Claims**

1. A photoelectric conversion device comprising a conductive support, a layer coated on the conductive support and containing semiconductor nanoparticulates having a dye adsorbed thereto, a gel electrolyte-containing layer, and a counter electrode, characterized in that

the gel of the gel electrolyte-containing layer contains constituent units of at least one type having a monovalent organic residue selected from among a carbonate group, a heterocyclic group containing a nitrogen atom, and a quaternary ammonium salt.

2. The photoelectric conversion device of claim 1, wherein the gel is a crosslinked polymer containing constituent units of at least one type having a monovalent organic residue selected from among a carbonate group, a heterocyclic group containing a nitrogen atom, and a quaternary ammonium salt.

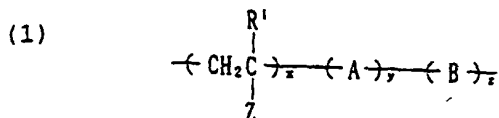
3. The photoelectric conversion device of claim 2, wherein the constituent units of the crosslinked polymer originate from an ethylenically unsaturated monomer.

4. The photoelectric conversion device of claim 3, wherein the ethylenically unsaturated monomer is at least one ethylenically unsaturated monomer having as a substituent a monovalent organic residue selected from among a carbonate group, a heterocyclic group containing a nitrogen atom, and a quaternary ammonium salt.

5. The photoelectric conversion device of claim 4, wherein said crosslinked polymer contains, in a weight compositional ratio, 5 to 99% by weight of recurring units originating from the ethylenically unsaturated monomer.

6. The photoelectric conversion device of claim 4 or 5, wherein said crosslinked polymer containing at least one type

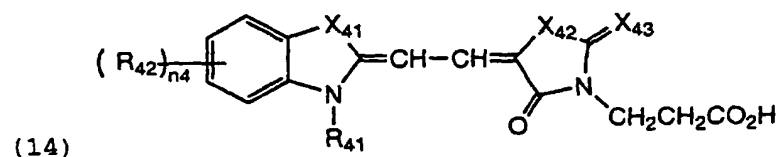
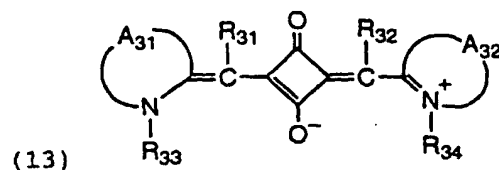
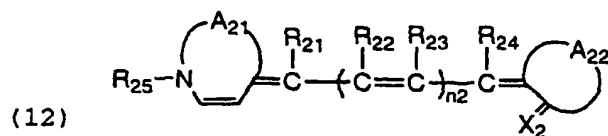
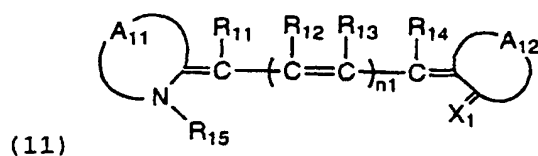
of recurring units originating from an ethylenically unsaturated monomer has the following formula (1):



wherein R<sup>1</sup> is hydrogen or alkyl of 1 to 4 carbon atoms, Z is a monovalent organic group containing a functional group selected from among a carbonate group, a heterocyclic group containing a nitrogen atom, and a quaternary ammonium salt, A represents recurring units derived from a compound containing an ethylenically unsaturated group, B represents recurring units derived from a compound containing at least two ethylenically unsaturated groups, letters x, y, and z represent weight compositional ratios of the recurring units associated therewith, respectively. x is from 5% to 99% by weight, y is from 0% to 70% by weight, and z is from 0.5% to 50% by weight.

7. The photoelectric conversion device of claim 6, wherein the ethylenically unsaturated monomer containing Z is at least one member selected from among ethylene glycol carbonate methacrylate, N-vinyl pyrrolidone, N-vinylloxazolidone, and N-vinyl-N'-ethylimidazolium iodide.
8. The photoelectric conversion device of claim 1, wherein said electrolyte is a metal iodide, an iodine salt of a quaternary ammonium compound, a metal bromide, a bromine salt of a quaternary ammonium compound, a sulfur compound, a viologen dye, or hydroquinone-quinone.
9. The photoelectric conversion device of claim 8, wherein said electrolyte is present in a concentration of 0.1 to 1.5 M.
10. The photoelectric conversion device of claim 9, wherein said electrolyte is a supporting electrolyte containing an iodine salt and/or a metal iodide.
11. The photoelectric conversion device of any one of claims 1 to 10, wherein the crosslinked polymer accounts for a weight fraction of 2% to 80% by weight of said gel electrolyte.
12. The photoelectric conversion device of any one of claims 1 to 11, wherein said gel electrolyte contains at least one organic solvent selected from among a nitrile compound, a carbonate compound, a nitrogenous heterocyclic compound, and an ethylene glycol dialkyl ether.
13. The photoelectric conversion device of any one of claims 1 to 12, wherein said gel electrolyte has been prepared by radical polymerization of a mixture containing a vinyl monomer, a polymerization initiator, a supporting electrolyte, and a solvent.
14. The photoelectric conversion device of any one of claims 1 to 13, wherein said dye is a ruthenium complex dye or polymethine dye.
15. A photo-electrochemical cell comprising the photoelectric conversion device of any one of claims 1 to 14.
16. A photoelectric conversion device comprising at least a conductive support and a photosensitive layer, characterized in that

said photosensitive layer contains semiconductor nanoparticulates sensitized with a polymethine dye of the following general formula (11), (12), (13) or (14):



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wherein in formula (11),  $R_{11}$ ,  $R_{12}$ ,  $R_{13}$ , and  $R_{14}$  each are hydrogen or monovalent substituents, or  $R_{11}$  to  $R_{14}$  may bond together to form a ring,  $R_{15}$  is alkyl,  $A_{11}$  and  $A_{12}$  each are a group of atoms to form a 3 to 9-membered ring with the carbon and nitrogen atoms,  $X_1$  is oxygen or sulfur,  $n_1$  is an integer of 1 to 4, the compound of formula (11) has at least one carboxyl group as a substituent, and the compound of formula (11) may have a counter ion depending on the overall electric charge of the molecule;

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in formula (12),  $R_{21}$ ,  $R_{22}$ ,  $R_{23}$ , and  $R_{24}$  each are hydrogen or monovalent substituents, or  $R_{21}$  to  $R_{24}$  may bond together to form a ring,  $R_{25}$  is alkyl,  $A_{21}$  and  $A_{22}$  each are a group of atoms to form a 5 to 9-membered ring with the carbon and nitrogen atoms,  $X_2$  is oxygen or sulfur,  $n_2$  is an integer of 0 to 3, the compound of formula (12) has at least one carboxyl group as a substituent, and the compound of formula (12) may have a counter ion depending on the overall electric charge of the molecule;

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in formula (13),  $R_{31}$  and  $R_{32}$  each are hydrogen or monovalent substituents, or  $R_{31}$  and  $R_{32}$  may bond together to form a ring,  $R_{33}$  and  $R_{34}$  each are alkyl,  $A_{31}$  and  $A_{32}$  each are a group of atoms to form a 3 to 9-membered ring with the carbon and nitrogen atoms, the compound of formula (13) has at least one carboxyl group as a substituent, and the compound of formula (13) may have a counter ion depending on the overall electric charge of the molecule;

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in formula (14),  $R_{41}$  is alkyl,  $R_{42}$  is a substituent,  $X_{41}$  is an alkylene group, alkylimino group, arylimino group, oxygen atom or sulfur atom,  $X_{42}$  is an alkylimino group, arylimino group, oxygen atom or sulfur atom,  $X_{43}$  is an oxygen or sulfur atom,  $n_4$  is an integer of 0 to 4, and the compound of formula (14) may have a counter ion depending on the overall electric charge of the molecule.

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17. The photoelectric conversion device of claim 16, wherein in the polymethine dye of formula (11), the heterocycle that  $A_{11}$  forms with the carbon and nitrogen atoms is benzothiazoline, indoline, naphthothiazoline or benzindoline.

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18. The photoelectric conversion device of claim 16 or 17, wherein in the polymethine dye of formula (11), the heterocycle that  $A_{12}$  forms with the carbon atoms is rhodanine.

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19. The photoelectric conversion device of any one of claims 16 to 18, wherein in formula (11), the carboxyl group is attached directly or via an alkylene group to the heterocycle that  $A_{12}$  forms with the carbon atoms.



**EP 0 911 841 A2**

20. The photoelectric conversion device of claim 16, wherein in the polymethine dye of formula (12), the heterocycle that A<sub>21</sub> forms with the carbon and nitrogen atoms is dihydroquinoline.
- 5 21. The photoelectric conversion device of claim 16 or 20, wherein in the polymethine dye of formula (12), the heterocycle that A<sub>22</sub> forms with the carbon atoms is rhodanine.
22. The photoelectric conversion device of claim 16, 21 or 22, wherein in formula (12), the carboxyl group is attached directly or via an alkylene group to the heterocycle that A<sub>22</sub> forms with the carbon atoms.
- 10 23. The photoelectric conversion device of claim 16, wherein in the polymethine dye of formula (13), the heterocycle that A<sub>31</sub> forms with the carbon and nitrogen atoms is benzothiazoline, indoline, naphthothiazoline or benzindoline, and the heterocycle that A<sub>32</sub> forms with the carbon and nitrogen atoms is selected from quaternary salts of benzothiazole, indolenine, naphthothiazole and benzindolenine.
- 15 24. The photoelectric conversion device of claim 16, wherein in formula (14), both X<sub>42</sub> and X<sub>43</sub> are sulfur atoms.
25. The photoelectric conversion device of any one of claims 16 to 24, wherein a steroid compound having a carboxyl group is adsorbed to the semiconductor nanoparticulates along with the polymethine dye.
- 20 26. A photo-electrochemical cell comprising the photoelectric conversion device of any one of claims 16 to 25, an electric charge transfer layer and a counter electrode.

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FIG. 1

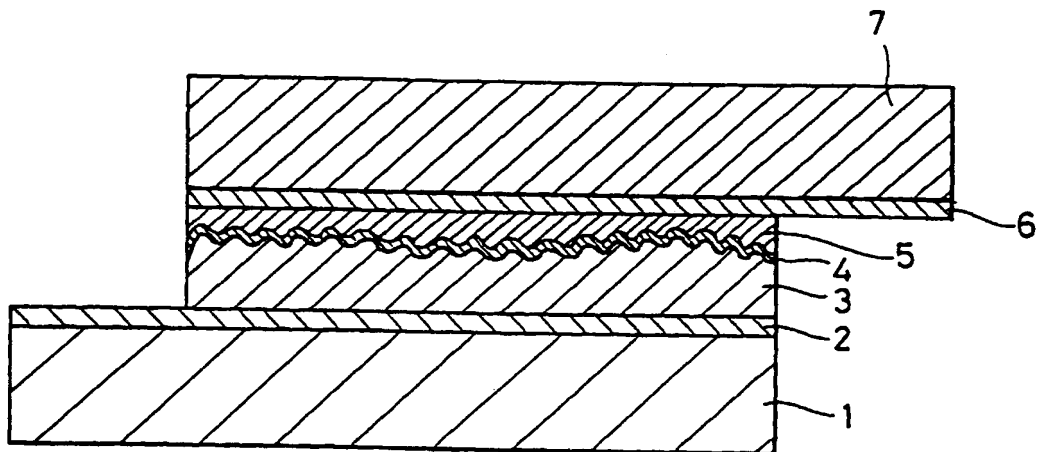


FIG. 2

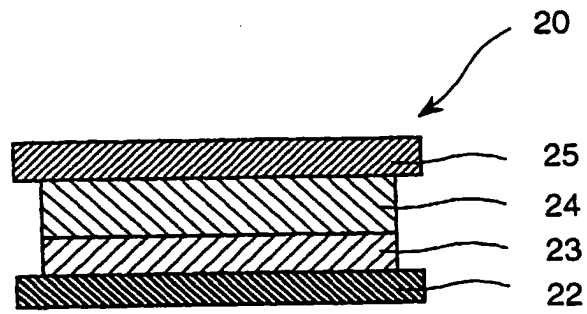
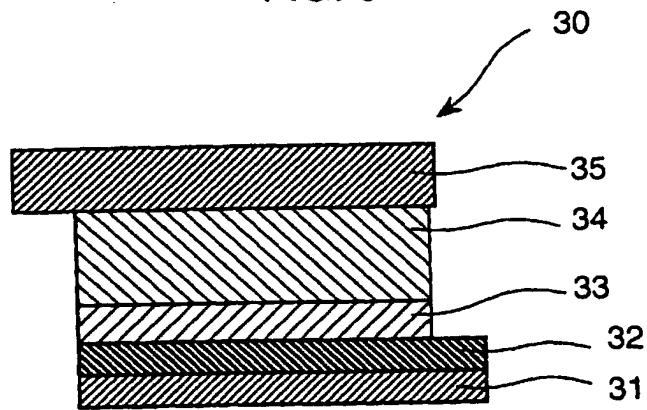


FIG. 3



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**EP 0 911 841 A3**

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(54) **Photoelectric conversion device and photoelectrochemical cell**

(57) A dye-sensitized photoelectric conversion device includes a conductive support, a dye-adsorbed semiconductor nanoparticulate layer, a gel electrolyte layer, and a counter electrode wherein the gel of the gel electrolyte layer contains constituent units having a carbonate group, nitrogenous heterocyclic group or quaternary ammonium salt. In another aspect, a photoelectric conversion device includes a conductive support and a photosensitive layer which contains semiconductor nanoparticulates sensitized with a specific polymethine dye.

**EP 0 911 841 A3**



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## EUROPEAN SEARCH REPORT

Application Number  
EP 98 12 0012

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Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.6)
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A	ITO K ET AL: "Ionic conductivity of poly(ethylene oxide) having charges on the chain end" SOLID STATE IONICS, vol. 79, July 1995 (1995-07), page 300-305 XP004050359 * page 301, column 1, line 32 - column 2, line 42 *	1-4	TECHNICAL FIELDS SEARCHED (Int.Cl.6) H01G H01L
D, A	MATSUMOTO M ET AL: "A dye sensitized TiO2 photoelectrochemical cell constructed with polymer solid electrolyte" SOLID STATE IONICS, vol. 89, no. 3-4, 2 August 1996 (1996-08-02), page 263-267 XP004069984 * page 264 *	1-3, 6-10, 13-15	
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 28 September 1999	Examiner Königstein, C
CATEGORY OF CITED DOCUMENTS X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document		T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document	

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# EUROPEAN SEARCH REPORT

Application Number  
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DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.6)
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A	YONEZAWA Y ET AL: "SPECTRAL SENSITIZATION OF SEMICONDUCTOR AND METAL ELECTRODES BY THE J-AGGREGATES OF CYANINE DYES: ENHANCED CATHODIC PHOTOCURRENT WITH THIACARBOCYANINE DYES HAVING MESO-PHENYL GROUPS" JOURNAL OF IMAGING SCIENCE, vol. 34, no. 6, 1 November 1990 (1990-11-01), pages 249-255, XP000172583 * the whole document *	16	
			TECHNICAL FIELDS SEARCHED (Int.Cl.6)
The present search report has been drawn up for all claims			
Place of search <b>THE HAGUE</b>		Date of completion of the search <b>28 September 1999</b>	Examiner <b>Königstein, C</b>
CATEGORY OF CITED DOCUMENTS X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document		T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document	

EPO FORM 1503 03 82 (90/01)



European Patent  
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## EUROPEAN SEARCH REPORT

Application Number  
EP 98 12 0012

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A	BUCKLEY R W: "AN INVESTIGATION INTO THE DEPLETION LAYER AND CARRIER PHOTOGENERATION IN MEROCYANINE - CDS PHOTOVOLTAIC CELLS" PROCEEDINGS OF THE INTERNATIONAL PHOTOVOLTAIC ENERGY CONFERENCE, FLORENCE, MAY 9 - 13, 1988, vol. 2, no. CONF. 8, 9 May 1988 (1988-05-09), pages 1028-1032, XP000044478 SOLOMON I;EQUER B; HELM P * the whole document *	16,18	
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E	EP 0 887 817 A (SHARP KK) 30 December 1998 (1998-12-30) * the whole document *	16	
A	EP 0 692 800 A (ISHIHARA SANGYO KAISHA) 17 January 1996 (1996-01-17) * column 8, line 3 - line 19 *		
The present search report has been drawn up for all claims			
Place of search <b>THE HAGUE</b>		Date of completion of the search <b>28 September 1999</b>	Examiner <b>Königstein, C</b>
CATEGORY OF CITED DOCUMENTS X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document			

EPO FORM 1503 (3.82 (P4/C01))



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Office

Application Number

EP 98 12 0012

#### CLAIMS INCURRING FEES

The present European patent application comprised at the time of filing more than ten claims.

- ☐ Only part of the claims have been paid within the prescribed time limit. The present European search report has been drawn up for the first ten claims and for those claims for which claims fees have been paid, namely claim(s):
- ☐ No claims fees have been paid within the prescribed time limit. The present European search report has been drawn up for the first ten claims.

#### LACK OF UNITY OF INVENTION

The Search Division considers that the present European patent application does not comply with the requirements of unity of invention and relates to several inventions or groups of inventions, namely:

see sheet B

- ☒ All further search fees have been paid within the fixed time limit. The present European search report has been drawn up for all claims.
- ☐ As all searchable claims could be searched without effort justifying an additional fee, the Search Division did not invite payment of any additional fee.
- ☐ Only part of the further search fees have been paid within the fixed time limit. The present European search report has been drawn up for those parts of the European patent application which relate to the inventions in respect of which search fees have been paid, namely claims:
- ☐ None of the further search fees have been paid within the fixed time limit. The present European search report has been drawn up for those parts of the European patent application which relate to the invention first mentioned in the claims, namely claims:





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**LACK OF UNITY OF INVENTION  
SHEET B**

Application Number

EP 98 12 0012

The Search Division considers that the present European patent application does not comply with the requirements of unity of invention and relates to several inventions or groups of inventions, namely:

**1. Claims: 1-15**

A photoelectric conversion device having a gel-electrolyte containing layer, characterised in that the gel-electrolyte contains constituent units of at least one of the following types: monovalent carbonate group, heterocyclic group with a N atom or a quaternary ammonium salt.

**2. Claims: 16-26**

A photoelectric conversion device having a photosensitive layer, characterised in that the photosensitive layer contains semiconductors nanoparticles sensitised with a polymethine dye.

EP 0 911 841 A3

**ANNEX TO THE EUROPEAN SEARCH REPORT  
ON EUROPEAN PATENT APPLICATION NO.**

EP 98 12 0012

This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report.  
The members are as contained in the European Patent Office EDP file on  
The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

28-09-1999

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For more details about this annex : see Official Journal of the European Patent Office, No. 12/82